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About the Keynote Speaker

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Isotropic Finishing of Helicopter and Turboprop Gearbox Components

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The traditional finishing techniques for engineered gearbox surfaces include but are not limited to hob shaving, gear grinding and honing. Regardless of the technique employed, a unidirectional polishing pattern is achieved as the final component surface finish. This pattern consists of parallel rows of asperities peaks that undergo fracturing and pulverization during the initial gearbox break-in period. This critical time results in high heat generation, high frictional force loading of the opposing engineered surfaces, metal chips in the lubricant and the initiation of future pitting or catastrophic metallurgical failure sites. By refining the engineered surfaces with an isotropic finishing process a final, non-directional surface finish is obtained. This isotropic finish requires no break-in, maintains cooler gearbox operational temperatures, generates no metal chips and most importantly, dramatically reduces the initiation of future pitting and/or metallurgical failure of gearbox components.

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Review of Traditional Gear Tooth Finishing Techniques

Helicopter transmission and turboprop gearbox components are typically cut from forged gear blanks by the use of traditional hob tooling. Hobbed gear teeth have an approximate final finish of 45-60 inches.

In an effort to produce a lower μ inch finish on the gear flank surface, gear teeth may be subjected to several sequential finishing operations. These operations typically include shaving, grinding, honing and diamond lapping. The final overall surface finishes achieved by each of these processes are detailed in Table 1.

Table 1			
Final Surface Finishes Achieved by Various			
Gear Tooth Finishing Operations			
Gear Tooth Shaving	35-60 µinches		
Gear Tooth Grinding	18-40 µinches		
Gear Tooth Honing	10-18 µinches		
Gear Tooth Lapping	$8 - 12 \mu$ inches		
	-		

Among the traditional finishing techniques used to produce low R_a finishes, most facilities still utilize gear tooth grinding. The use of grinding wheels containing specific grades of aluminum oxide results in a specific overall finish. By sequencing successively finer grades of aluminum oxide grinding wheels, successively smoother overall final finishes can be obtained. See Table 2.

	Table 2
Normal Succession	of Gear Tooth Grinding Wheels
Wheel grit grade	Resultant overall surface finish
180 grit wheel	20-25 µinches
220 grit wheel	18-20 µinches
240 grit wheel	15-18 µinches
300 grit wheel	12-15 µinches

Photo 1; (below)

This photo is a close-up view of a bevel gear showing grind line patterns left in the flanks of the gear teeth following a gear grinding operation.





Shows a 3-dimensional view of the topography of a gear tooth that has been refined ($R_a = 35 \mu$ inches) using a traditional gear grinding technique. Note the successive rows of resultant asperities corresponding to the directional pattern of the gear grinding operation.



In a gear tooth honing operation, an abrasive hone in a conformational form is rolled across the gear flank in a crossed axis pattern. Since the hone contains abrasive particles, it imparts а mechanically smoother finish to the gear flank corresponding to the size of the abrasive used to prepare the honing tool. The traditional honing operation is a wet process. An appropriate fluid is used as a lubricant and a coolant. A moderate flow rate is applied to flush away the resultant honing swarf.

Diamond lapping requires components such as transmission rings and pinions to be mated then run to break-in the components prior to final assembly. Essentially, the break-in phase for new components is accomplished at the manufacturing facility rather than in the customer's gearbox.

During diamond lapping the only asperities that are removed are those that are abraded at the contact points of the engaged teeth. A disadvantage to the diamond lapping technique is that lapped components must remain as matched pairs through subsequent handling operations and then final assembly. This adds a complexity to the manufacturing operation that would be better eliminated if the components could be refined in bulk then randomly combined during final assembly.

Regardless of the traditional technique used to produce the final surface finish, the overall intent of any of these finishing procedures is identical, to produce a consistently lower R_a finish on the gear tooth, than is generated during the initial gear hobbing operation.

Generating the Isotropic Finish

According to several published articles^{3,8,12} metal contact surfaces. refined with chemically accelerated vibratory finishing techniques^{5,6} have a superior final finish. This is due to the asperities having been chemically refined and not mechanically abraded from the surface of the engineered component.

Figure 2; (below)

Shows a 3-dimensional view of an isotropically produced surface finish ($R_a = 1.5 \mu$ inches) generated by the techniques as described in^{5,6,7}. Note the elimination of all asperities has improved the topography of the final gear tooth surface. The remaining low areas provide sufficient recesses for good lubricant retention.



According to the techniques described by^{5,6,7} asperity refinement occurs in a chemically accelerated vibratory finishing process. The gears to be refined are placed into a vibratory bowl containing a high-density, non-abrasive media⁶. The process involves two steps.

The initial step is the refinement process, wherein a chemical interaction takes place on the surface of the part⁷. A thin (1 micron) film is formed on the part surface that is soft by nature. Through the interaction of the media in the vibratory system, the "film" is physically removed from the "asperities" of the part⁷. Since the "valleys" are recessed and untouched by the media, the film remains untouched and the valleys are unaffected⁷. The chemical "film" then reforms only at the surfaces interacting with the vibratory media and the process repeats itself⁷. As a function of time, the "asperities" are removed, leaving only the valleys, thereby, generating the improved micro-finish⁷.

The second step is referred to as the burnish process. After the required micro-finish is achieved, a mild alkaline mixture is introduced⁷. After a relatively short period, a mirror-like polished finish is produced⁷. Additionally, this step removes any residual film remaining from the initial refinement step. Cost savings are realized through the ability to process parts in mass, thereby, producing a superior isotropic finish at per piece costs lower than conventional machining/grinding operations.

Photo 2: (below)

Shows a chemically accelerated vibratory produced isotropically finished bevel gear ($R_a = 1.5 \mu$ inches) with all asperities removed.



Analysis work⁴ has shown that the process chemistries used in this technique produce no metallurgical degradations such as hydrogen embrittlement. This technique is a proven robust production process and can maintain gear tooth accuracy within an AGMA 14 quality number.

Benefits of the Isotropic Finish Improved R_{sk}

Some authors¹² refer to the resultant surface as a *No Run-In* surface. An asperity free, final surface is critical to extended gear tooth performance as is noted in ^{3,8,12} since the R_{sk} of the engineered surface has been improved. The skewness, i.e. R_{sk} , is a measurement of the asymmetry of the surface profile about the mean surface position. A positive skewness indicates that the most distant lying points on a surface. A negative skewness indicates the most distant lying points are proportionately above the mean surface.

Figure 3; (below)

Shows a profilometer tracing of an as ground engineered surface with an $R_a = 18.94$ inches and an $R_{sk} = -0.0949$. Note: asperities extend upward and valleys extend downward.



Examining Figure 3, shows the initial surface has an R_{sk} near zero. There is an approximately equal distribution of asperities above and below the mean surface of the part.

Figure 4; (below)

Shows a profilometer tracing of an istropically finished surface with an $R_a = 5.77$ inches and an $R_{sk} = -3.0968$. Note: no asperities remain above the mean part level. Since only recessed valleys remain the R_{sk} skew has been dramatically improved to a -3.0968.



By isotropically removing asperities from tooth surfaces, the R_{sk} is approximately -3 showing that the asperities were refined. This is important because all loading on this surface was previously carried by only a few of the highest asperities on the ground surface. The isotropic surface produced by the chemically accelerated vibratory finishing technique generated an asperity free surface, which effectively disperses the load across a wider area, thereby, reducing stress in any one location.

This phenomenon was clearly demonstrated in a 1994 evaluation¹² on roller bearing contact surfaces. The evaluation¹² graphed a 2.5 to 1 reduction in Hertzian stress associated with the asperities found on a traditional ground bearing surface when compared to an identical bearing surface that had been isotropically refined. Measured¹² Hertzian stress levels at surface contact asperities were found to be as high as 1.12 GPa. The authors¹² defined a 0.93 GPa Hertzian stress upper limit to asperities prior to plastic deformation. Measured¹² Hertzian stress levels for identical, isotropically refined bearings were a uniform, 0.45 Gpa.

Reduced Wear and Contact Fatigue Pitting

As discussed previously, traditional shaving, grinding, honing, and lapping techniques do not eliminate asperities; rather, they replace them with more rows of shorter asperties. Parts with this type of overall starting condition, when placed into operation for the first time, undergo a break-in period as noted by^{3,8,12}. During break-in and during the normal operation of gears, asperities undergo intense plastic deformation¹², wear, and contact fatigue. Gears that undergo this type of operation experience certain surface degradation problems:

- 1. Snapping off of asperities results in the formation of a pit or hole at the former interface of the asperity base and the gear tooth surface.
- 2. A snapped off asperity becomes metal debris and is carried through the gearbox where it is interspersed between engaged gear teeth. As the asperity debris is pulverized, it generates further surface

damage in the form of pits and gouges on the surface of gear teeth with which it has been interspersed.

Photo #3; (below)

Shows gear tooth spalling caused by surface pit propagation. The gear shown was finished using traditional gear grinding techniques. Asperity wear during the gear break-in phase produced pits, which coalesced into irregular craters over a significant area of the gear tooth.



By preventing the generation of contact fatigue initiation sites, gear tooth durability is dramatically improved. Recent testing^{2,9} has shown that isotropically finished discs resist scuffing damage at loading levels two to three times greater than traditionally ground discs.

Ring and block evaluation work⁸ has shown a 22 to 1 decrease in the amount of metal wear as a direct result of the application of an isotropic finish. In this evaluation⁸ sets of blocks were processed to generate a traditional ground surface and an isotropic surface. The blocks were weighed and fixtured against a ring that was rotated at 800 rpm for 6 hours. The blocks were then measured for the wear patterns produced and metal loss generated. The test showed a significantly higher volume of metal wear associated with the traditional ground surface. See Figures 4 & 5. Asperity wear and the resultant pit generation fostered a snowballing rate of metal wear.

Additional independent work¹⁰ confirmed minimal metal removal during gear tooth refinement to generate an isotropic finish. Measurements¹⁰ of stock removal during the isotropic finishing process showed that a minimal stock removal; 0.00012",

was necessary to impart an isotropic finish, thereby, assisting a manufacturing operation to maintaining close machining tolerances.

Figure #4; (below)

Figure #4 shows the wear pattern produced in a ring-and-block evaluation⁸ on a traditionally ground steel block.





Figure #5 shows the wear pattern produced in a ring-and block evaluation⁸ on an isotropically finished steel block. The result of this evaluation produced 22 times less metal removal as was produced in the coupon shown in Figure #4.

Lower Operating Temperatures

Break-in periods for gear teeth and assorted engineered surfaces can easily be monitored by the temperature spike generated during the break-in procedure^{3,8,11,12}. See Graph #1. Isotropically finished components require no break-in period since the starting surface is already smooth, therefore, there is no temperature spike. See Graph #1. Work done by^{1,3,8,11,12} additionally demonstrates a significant reduction in continual operational temperature for isotropically finished components. See Graph #1.

Graph #1; (below)

Shows the traditional break-in temperature curve with a temperature spike for a ground surface finish versus an isotropically finished surface, which shows no corresponding temperature spike⁸.



Examination of this graph shows that isotropically finished components have a gradual rise to a plateau operating temperature of 133°F. Traditionally ground components have a temperature spike at 165°F prior to equilibrating at a consistent operational temperature of 150°F. In this evaluation⁸, isotropically refined engineered surfaces had a durational operating temperature of 17°F less than standard ground surfaces. This represents a 13% reduction in overall operational temperature.

Reduced Frictional Force

In a recent evaluation², pairs of ground and pairs of isotropically refined discs were rotated against each other in a high speed, scuffing rig. The rig allowed evaluators finite control over disc rotational frictional forces. The test evaluators could precisely increase and monitor the increased frictional forces applied to the discs until engineered surface failure; (i.e. scuffing) occurred. Additionally the rig's oil sump was equipped with a thermocouple that allowed evaluators to monitor the operating temperature of the disc sump environment².

The evaluation² showed that during high speed rotational testing; designed to simulate the sliding speeds considered typical of an aerospace gearbox -26 m/s, traditionally ground discs failed at a force loading of 1,850 N whereas isotropically finished discs failed at a force loading of 4,150 N. This represents a 2.25 to 1 increase in disc durability. Simultaneously, the measured frictional force on the discs² showed that the traditionally ground discs had risen to 54.2 N as opposed to 46.5 N for the isotropically refined discs. This represents an approximate 16% reduction in the frictional force between the discs.

Monitored² temperature in the rig was 240°C for traditionally ground discs and 201°C for isotropically finished discs. This represents, a 16% reduction in oil sump temperature for the rig.

Similar testing¹ was conducted on traditionally ground and isotropically refined gears. The result of this testing was nearly identical to the disc evaluation² discussed above. When both gear types were tested at identical rotational speeds of 5,000 rpm, the authors¹ reported a 30% reduction in frictional torque as a result of isotropic finishing when compared to traditional ground gears. The authors¹ also noted a 10.5% reduction in the operational temperature of the rig's oil sump.

Benefits to Helicopter and Turboprop Gearbox Components

Improved R_{sk} means that components with an isotropic finish produced by the chemically accelerated vibratory process will exceed the engineering demands required current of traditionally finished components. This suggests the possibility of using smaller components in the gearbox to safely operate at higher power densities. Smaller components mean less mass and, therefore, less weight to be lifted. Since the mass of weight to be lifted can be reduced, payload efficiency can be increased.

Lower operational temperatures mean cooler helicopter and turboprop gearboxes. Since heat is a horsepower thief, maintaining a cooler gearbox is an effective way of creating a power increase. In the gear evaluation discussed previously¹, the authors note that "although the overall gain in efficiency of power transmission of the gears as a result of these improvements are small, the reduction in total losses, if realized in high-power reduction gears for an aircraft engine geared–fan drive, for example, could be of significant benefit in terms of the reduced cost, weight and aerodynamic penalty of cooling equipment."¹ This is an incredible benefit in the potential reduction in weight caused by eliminating or greatly downsizing lubricant cooling units aboard an aircraft and can be effectively multiplied across aircraft with multiple engines and gearboxes.

Reduction in engineered surface Hertzian contact stresses¹² reduces plastic deformation of the surface¹² asperities, thereby reducing wear and contact fatigue pitting. Since failures are exacerbated by the presence of an initiation site, eliminating these sites will foster greater component durability^{2,9} and dramatically reduce replacement of gearbox components⁸. Greater gearbox durability can be directly related to lower maintenance costs and lower downtime for the aircraft.

Generating an isotropic finish on gearbox components will reduce the frictional torque required to rotate the components¹ thereby generating greater horsepower and fuel economy. Both are significant advantages to increasing payload efficiency of the aircraft.

Conclusion

In general, if two reciprocal engineered surfaces operate by sliding, rolling, meshing or pushing against each other, component performance and durability for the pair will be significantly enhanced by generating an isotropic final finish on the surfaces. Since the isotropic finish is applied with a chemically accelerated vibratory technique the surface improvement can be generated quickly and cost efficiently in a mass production method. Benefits of isotropic surface finishes have been noted as:

- 1. Improved R_{sk} between the reciprocal surfaces.
- 2. Reduced operational temperatures for reciprocal components and lubricant.
- 3. Reduction in the frictional force between reciprocal components.
- 4. Reduction of the torque required to rotate finished components.

- 5. Reduction of metal wear on reciprocal components.
- 6. Increase in gear tooth resistance to contact fatigue pitting.

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Jet Engine Overhaul Environmental Management System 14001

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Lufthansa Airmotive Ireland received an Integrated Pollution Control License (IPC) from the Irish EPA in January 1999. To fulfill the requirements of the license, the company was required to establish an Environmental Management System (EMS). The EMS was required to assess all operations plant-wide and to review all options for the use of cleaner technology, cleaner production and the reduction and minimization of waste. The company received the ISO 14001 Environmental International Standard in April 2000, the award was formally presented by the Minister of the Environment in July 2000. This presentation will discuss the environmental management programs that have been established and the cleaner technology processes that are being commissioned for the repair and overhaul of jet engine components.

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Introduction

The Environmental Protection Agency (EPA) is the statutory body in Ireland with responsibility for issuing Integrated Pollution Control (IPC) Licenses to businesses and industrial organisations within the country. Lufthansa Airmotive Ireland was granted an IPC Licence in 1999 which sets out the conditions, programmes and operating procedures to be implemented in the areas of:

- ♦ Waste Water
- ♦ Air Emissions
- Noise Emissions
- ♦ Hazardous And Non-Hazardous Waste

One of the important requirements set out in the license is the implementation of an Environmental Management System (EMS) which will assess all operations and review all practicable options for the use of cleaner technology, cleaner production and the minimisation of waste.

Management Of The Activity

The ISO 14001 Environmental Management System (EMS) which is an internationally recognised standard was the vehicle adopted to manage and control the overall environmental performance of the company. Additionally customers within the Jet Engine Overhaul industry now recognise the importance of environmental management control and accreditation to an International Standard is becoming increasingly necessary.

Environmental Policy

In an Environmental Policy Statement the following principles have been adopted:

- ♦ To document and evaluate the environmental impact of our activities.
- ◊ To review objectives and targets aimed at continual improvement of environmental performance by utilising cleaner technologies and process substitution where possible.
- To put in place structures to monitor and minimise our environmental impacts.

- ◊ To conform to all statutory requirements set out in our IPC License.
- ◊ To promote Environmental Awareness among all our employees.
- ◊ To ensure this Environmental Policy is available to the public.

Environmental Aspects

A Register Of Environmental Aspects which identifies all activities that interact with the environment was compiled. An activity is considered an environmental aspect if it can interact with the environment and the company has an influence over the activity. The Register is regularly reviewed and updated when a new process or activity is considered.

Significance Rating

The significance of an environmental aspect was based on simple risk methodology and the method of calculation was used to establish a significance rating for each aspect.

The significance rating is calculated as follows:

$\underline{\mathbf{C} = \mathbf{F} \mathbf{x} \mathbf{L} \mathbf{x} \mathbf{S}}$

|--|

- F = Frequency of Occurrence of the aspect and a numerical value between one (i.e. rare) and 10 (i.e. regular/consistent) is assigned.
- L = Loss of control and a value between one and ten is assigned where one indicates control loss is unlikely and ten indicates control loss is highly likely.
- S = Severity of consequences and is assessed using the following criteria:
- (1) Legislative and Regulatory Compliance
- (2) Community/Employee Sensitivity
- (3) Impact on Air, Land, Water
- (4) Cost benefit reasons e.g. insurance liability
- (5) Potential for resource depletion
- (6) Accident and Emergency

The criteria (1) to (6) is scored between one and five, dependent upon the risk:

e.g. one indicates no risk and five indicates intolerable risk.

Using the subject criteria the top five environmental impacts in order of significance were:

- Emissions to Atmosphere
- Environmental Noise
- ♦ Hazardous Materials
- ♦ Non-Hazardous Waste
- ♦ Hazardous Waste

Objectives And Targets

The Register of Aspects identified five main objectives which have become the main focus in terms of implementing cleaner technologies, cleaner production and waste minimisation. These objectives have resulted in the following targets now being implemented:

- Eliminate use of Trichloroethylene by July 1st 2001.
- Eliminate use of Solvents in Bearing Cleaning by July 1st 2001.
- ♦ Reduce Noise Emissions from the site.
- Minimise use of Hazardous Materials by July 1st 2001.
- ◊ Reduce quantity of Non-Hazardous Waste to landfill by December 2000.
- Develop Waste Minimisation Strategies for hazardous waste throughout the production process over the next five years.

Trichloroethylene Replacement

Spray Wash Machines

Vapour degreasing using Trichloroethylene has been the standard process used in the engine overhaul industry over many years. This has been a 'One-Step' process where the resulting parts were:

♦ Clean

♦ Dry

No Surface Residues

Spray wash machines, Figure 1, using a water based alkaline detergent has been adopted as the alternative process to vapour degreasing. The process steps are integrated in one chamber within the machine and in one fully automatic cycle e.g. parts are not moved from tank to tank. The machine is fitted with a cell to convert incoming tap water to de-ionised water for processing.

An oil skimmer and filtration system is also embodied in the machine and the entire process is fully programmable.



Figure 1 - Spray Wash Machine

Dedicated Processes:

The substitute process is located in these areas of the plant where trichloroethylene has been the historical degreasing process e.g:

- Degreasing prior to coating e.g. plasma, plating, painting
- 14 ♦ Degreasing prior to FPI
 - A Degreesing nost MPI

◊ General removal of oil and grease from engine parts

The parts requiring degreasing in the high pressure spray wash machines are processed as follows:

- Spray wash in water based Alkaline detergent at a concentration of 3% to 5% x 4 5 minutes
- ♦ Re-Circulate chemical to process tank x 2 minutes
- ♦ Hot Rinse (De-Ionised Water) at 80°C x 3 4 minutes
- ♦ Water removal by vacuum if required
- \diamond Hot Air Dry (120°C) x 5 6 minutes
- ♦ Total cycle time is approx. 15 minutes

The rinsewater will be discharged to drain under controlled conditions based on chemical analysis and parts thru-put. Contaminated degreasing solutions will be dumped to drain or routed for waste disposal in accordance with the requirements of our IPC licence.

Removal Of Plating Wax

The removal of residual wax which remains on jet engine components after de-waxing in hot water has been traditionally carried out using vapour degreasing in trichloroethylene.

A semi-aqueous process for removing plating wax using the n-Propyl Bromide free product will be installed in the plating shop. The new process line will embody hot rinsing stages before and after a chemical de-wax and also an alkaline rinse aid. A schematic of the new de-wax line is shown in Figure 2.

The chemical de-wax product is expensive and methods of extending the life of the process will be investigated. Some shops dump the process on an annual basis but this will depend on thru-put and shops experience.



Figure 2 - Trichloroethylene Replacement Dewaxing Plating Process

Solvent Replacement

Bearing Cleaning

The elimination of solvents in the cleaning of engine bearings was identified as a key objective in the Register of Aspects particularly with respect to Air Emissions.

An Aqueous based cleaning process has been adopted as the alternative process to solvent cleaning. The bearings will be processed in a semi automatic system using a water based alkaline cleaner followed by cold rinsing dewatering and preservation. (Fig 3)

A facility for ultrasonic cleaning will be installed in the process solution if necessary.

Mechanical agitation will be provided at each processing stage. The bearings will be inspected in the presence of the dewatering oil and preserved in preservation oil for long term storage if required.

Aqueous Cleaning of Engine Bearings





Figure 3 - Solvent Replacement Aqueous Cleaning of Engine Bearings

WASTE MINIMISATION

Non-Hazardous Waste

Strategies have been developed within the company to minimise non-hazardous waste streams historically routed to landfill. Recyling programmes are now in place for the following waste streams:

- Waste paper is collected, weighed, shredded and baled for recycling to paper mills.
- ♦ Waste cardboard is either re-used or if nonuseable is recycled.
- ♦ Waste timber e.g. pallets or boxes is collected, shredded and recycled.

Non-Hazardous Process Waste:

- Aluminium Oxide is recycled and re-used for surfacing grinding wheels.
- Plasma Dust Nickel is extracted from the metal dust and is re-used commercially.
- \diamond Steel Shot Routed to steel mills for scrap.

WASTE MINIMISATION

Hazardous Waste

Hazardous waste is primarily generated from the following waste streams:

- Alkaline and Acid solutions from chemical cleaning processes.
- ♦ Acid and Alkaline solutions (Cleaners and Strippers) from Electroplating processes.
- Chlorinated and non-chlorinated solvents from cleaning and inspection processes.
- ♦ Empty chemical packaging.
- ♦ Time expired consumables.

The following programmes are being examined to reduce waste and reduce our dependence on waste disposal contractors:

- Extend the life of cleaning process solutions using filtration techniques (Tanks are currently dumped annually).
- ♦ Upgrade our Effluent treatment capability.
- ♦ Return empty packaging to suppliers.

Reduce quantity of time expired waste consumables by adopting the following measures:

- ♦ Re-Qualification for further life extension.
- ♦ Tighter control of inventory stock.
- ♦ Review of purchasing policy.

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Deep Cryogenic Treatment of Materials for Aerospace Applications

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The results of Rolling/Sliding Contact Fatigue (R/SCF) tests were compared for two aerospace carburizing heattreatment processes. All samples were from one heat lot of AMS 6265J (Single Vacuum Melted SAE 9310H) gear material. The material was normalized, quenched, tempered, carburized, subcritical annealed, copper plated, quench hardened, tempered, copper stripped, ground and surface temper inspected to conventional aerospace specifications. All samples were processed in the same heat treat lot. Some were randomly selected as the baseline process for testing. Others were given an additional deep cryogenic treatment (-320°F) and temper after grinding. The following are presented: R/SCF test results (with end-of-test pit appearance criteria), metrological changes, microstructural changes (the presence of eta carbides and microcracking), and temper resistance behavior. Recommended heat treatment and cryogenic treatment processing specifications are included in the paper with a discussion of the benefits of tempering prior to deep cryogenic treatment. Eddy current examination and use of the Barkhausen Effect are discussed as test methods for confirming cryogenic processing. Also discussed in this paper are other potential benefits of cryogenic treatment for carburized gear materials such as cryogenic stress relief. Recommendations are given for additional work in this area.

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1 Introduction

During the heat treatment of steel parts, it has been a normal practice to include a -120°F cold treatment cycle. This process is performed after the austenitic steel is quenched, but before it is tempered. This process is performed to transform the remaining austenite in the quenched part into martensite. Martensite improves the wear characteristics and hardness of finished steel.

In recent years, devices for precisely controlling the temperature of components at -320°F have become available. This has allowed experimenters to evaluate the effect of cryogenic processing on heat treated steels. The cryogenic treatment of steel products has become a controversial process. Claims of improvement in performance properties and part life for cryogenically processed steel components have been made since the early 1940's. These testimonials to the improved properties of cryogenically treated components have been met with counter claims that the process does not always result in improved properties.

In the former Soviet Union, a cryogenic process referred to as "Shock Cooling" was developed to process steels. The steel was lowered into a bath of liquid nitrogen and held there until the part reached equilibrium (temperature); the steel was then allowed to return to room temperature. The materials that were treated included stainless steels and molybdenum alloy steels. It was claimed that the process improved the wear characteristics of the steel and the practice of treating steel with the Shock Cooling method became a widespread application in over 100 enterprises. Between 1977 and 1978, the State Committee on Patents and Discoveries in the Soviet Union determined that while there was considerable savings gained through the cryogenic process, the results were not consistent. In the survey taken, it was determined that only 70% of the 204 enterprises evaluated were obtaining consistent results.¹

Additional development work on the cryogenic process and its control was performed in Great Britain. The process developed in Great Britain eliminated the possibility of thermal shock that could occur in the Shock Cooling process. This was accomplished by pre-cooling the steel prior to immersion into the liquid nitrogen. After removal from the liquid nitrogen, the steel was allowed to return to room temperature in air.²

In Canada, research by private corporations has been undertaken with the support of the Canadian Industrial Research Assistance Program. This research has developed a cryogenic process that has produced claims of improvements in wear from 40 to 300%.³

Research efforts were performed in the United States at the Louisiana Technical Institute to determine the effect of cryogenic exposure time on wear resistance properties in steel components. This study determined that holding steel at a temperature of -310°F for a period of over 20 hours would result in a component with improved wear resistance.⁴

2 Experimentation

2.1 Investigation

Experimentation was conducted at IIT Research Institute's "Instrumented Factory for Gears" Heat Treatment facility, which has a state-of-the-art Honeywell computer control system. This system has the capability of controlling the cryogenic chamber ramp-down at 20°F/hour. The chamber itself is equipped with a circulating fan that can operate at -320°F. Dual control-solenoid-valves eliminate the possibility of frozen controls during extended cycles. The carburization furnace heat zone is controllable to within $\pm 3^{\circ}F$ between the operating temperatures of 1475°F and 1700°F. This precision was verified using a standard nine-point survey.

The purpose of this experiment was to determine the effect of the cryogenic process on the material and any resulting material property improvements due to the process.

Changes in pitting resistance and temper resistance due to cryogenic processing were investigated. Changes in the pitting resistance of a cryogenically treated material correspond to changes in the wear characteristics of the material. Temper resistance was examined to see if cryogenically treated materials could withstand a higher-temperature environment than conventionally treated materials. Improvements in temper resistance would improve resistance to softening due to exposure to high temperature environments and would result in the ability of parts to withstand a more severe operating environment.

2.2 Methodology

This project began with a review of previous work in cryogenic treatment. A process was selected, and AMS 6265J (Single Vacuum Melted SAE 9310H) was chosen as the material of interest. A baseline utilizing the existing conventional hardening process was established and then compared to the results of the cryogenic process. The conventional process utilizes a standard cold treatment (-120°F). The cryogenic process was designed such that results would be obtained from both a pre-temper and a post-temper cryogenic cycle.

The selected method of testing for pitting resistance was the Rolling/Sliding Contact Fatigue (R/SCF) test. The selection of this test required that the material be machined into a set of mating parts consisting of a pin and a disk. This configuration was used for both the pitting resistance and temper resistance evaluation.

After machining the parts into the required pins and disks, they were normalized (to relieve any machining stresses). Normalization was accomplished by heating the material above its upper transformation temperature and slowly cooling the parts to room temperature. After normalization, the parts were reheated to 1500°F in a controlled-atmosphere integral-quench furnace, quenched in oil (120°F) and tempered at 300°F for three hours.

The material was carburized at a temperature of 1700°F to obtain a case depth of 0.040 in. The furnace was lowered in temperature to 1450°F and the parts were stabilized for one hour. The material was then allowed to cool in the furnace vestibule. Following this, the material was sub-critical annealed at 1175° F for three hours.

Randomization was utilized for division into a baseline lot and multiple cryogenic lots.

The parts were copper plated to a thickness of 0.001-0.002 in. prior to performing the hardening cycle. A controlled atmosphere integral quench furnace was used to austenitize the parts ($1500^{\circ}F$) for two hours. The parts were then quenched in oil ($120^{\circ}F$). The baseline and post-temper cryogenic lots were given a cold treatment ($-120^{\circ}F$) for two hours and were tempered at $300^{\circ}F$ for three hours. The pre-temper cryogenic lot was given a cryogenic treatment ($-320^{\circ}F$). The cool down ramp was controlled at 20° F/hr. The parts were held at that temperature for a period of 20 hrs. The parts were returned to room temperature at a rate of $20^{\circ}F$ /hr and then tempered at $300^{\circ}F$ for two hours.

The post-temper cryogenic lot was given a cryogenic treatment (- 320° F). Ramp-down was controlled to 20° F/hr and the material was held at temperature for 20 hrs. The parts were returned to room temperature at a rate of 20° F/hr and then tempered at 300° F for two hours.

After heat treatment, the copper plating was stripped and the parts ground to their final configuration. A surface temper etch inspection was performed to ANSI/AGMA 2007-B92 and ISO14104: 1995 specifications.

3 Results and Discussion

The parts were evaluated for retained austenite and residual stress by means of x-ray diffraction. Both the baseline and cryogenic lots exhibited similar retained austenite and residual stress. The retained austenite was measured at between 6.0-7.4%. Residual compressive stress was measured at between 77-88 ksi.

The microstructure of the baseline lot and the post-temper cryogenic lot was examined at a magnification of 30,000X using a SEM. The microstructure of each lot was similar with no noticeable differences. The parts were also evaluated for evidence of microcracking and none was found.

R/SCF tests were used to evaluate the wear characteristics of the baseline and post-temper cryogenic lots. The results of these tests are illustrated in Figure 1. Comparison between the baseline and the post-temper cryogenic lots demonstrates that the post-temper cryogenically treated components have a 50% extra pitting resistance life and have a 5% greater load carrying capacity. The cryogenically treated parts achieved a life of 7.42 million cycles compared to the baseline parts, which achieved a life of 4.9 million cycles. The tests were at a load of 400 KSI and 43% slip. The results of the retained austenite measurements indicate that the improvement is not a result of retained austenite being transformed into martensite.



Rolling/Sliding Contact Fatigue (R/SCF) Life

Figure 1 – Results of R/SCF tests performed on the baseline and post-temper cryogenic lots.

Research performed at the Iron and Steel Institute of Japan (ISIJ) supports this interpretation. The ISIJ study indicated that material performance could be improved without reducing retained austenite. This is accomplished through martensitic decomposition, formation of *h*-carbides, reduction of *e*-carbides, and a resultant finer martensitic structure.⁵

Temper resistance of the baseline, pre-temper cryogenic, and post-temper cryogenic lots was evaluated. Rockwell-C Hardness (HRC) was used as the response variable, and was checked on a calibrated Wilson hardness tester. The hardness readings of the parts were taken "as received," and were also taken after the

Cryogenic treatments were performed. Parts from the post-temper lot and the pre-temper lot were further tempered at increasing temperatures in increments of $25F^{\circ}$, and the resultant hardness readings were recorded.

The data from the temper resistance evaluation indicates that cryogenic treatment improves the temper resistance of the treated steel. The analysis indicates that the pre-temper cryogenic treatment creates a greater improvement than the post-temper cryogenic treatment. The pre-tempering cryogenic treatment was able to withstand temperatures between 40 and $60F^{\circ}$ more, to effect the same reduction in hardness. The results of the temper resistance evaluation are shown in Figure 2.



Figure 2 – Results of the temper resistance evaluation.

In an attempt to identify and distinguish between the effects of the cryogenic treatment, two evaluation methods were investigated: Eddy Current and Barkhausen Noise Analysis.

Eddy Current is a non-destructive test that has successfully been used to identify cracks in material and differences in heat treatment processes. The inspection method relies on the inducing of "eddy currents" in the material to be inspected. This is accomplished by bringing a coil with alternating current flowing through it into contact with the material to be tested. The voltage is monitored across the coil. Interruptions in the eddy current flow in the material being tested will change the loading on the coil by increasing or decreasing the effective impedance and this will effect a change in the instrument voltage.

The Barkhausen Noise Inspection method is used to detect grinding damage in gears. This relies on locating a magnetizing field near a ferromagnetic material. The field causes the material to undergo a net magnetization change. This change is a result of a microscopic movement of magnetic domain walls in the material. When the change occurs, a detectable electrical pulse is given off that can be compared against a measured standard.

The Eddy Current and Barkhauser test methods require that a standard be utilized as a baseline for examining differences. Several unsuccessful attempts were made to identify a standard for either method that would consistently identify cryogenically treated components. The failure to identify a standard for either evaluation method has prevented their use as a means to obtain data from the cryogenic treated parts.

4 Recommendations for Future Work

Additional evaluations are underway at IIT Research Institute in this area of study. A project investigating the effect of cryogenic treatment on stress relief and wear in Heat Treated SAE 4130/4140 steel tubes is just getting underway. Initial results indicate that cryogenic treatment of this steel can relieve stress due to manufacturing. Other areas of concern include:

- A method of identifying material that has been cryogenically treated and of quantitatively measuring the condition of the material needs to be developed.
- Efforts should be made to investigate the effect of combining Deep Cryogenic treatment with improvements in surface finishing and surface coating treatments.
- A sensitivity analysis needs to be performed on the process and materials to identify the most significant factors affecting these phenomena and to explain the mixed performance results often reported. This analysis will utilize the unique Laser Gas Analyzer recently installed on the atmosphere control system.

5. Conclusions

The following conclusions are drawn from the study:

- Cryogenic treatment improves Rolling/Sliding Contact Fatigue life.
- Cryogenic treatment improves temper resistance.
- Non-destructive testing did not distinguish the different in processes. The inability to identify and establish a measured standard restricted their usefulness.

6. Acknowledgements

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The R/SCF tests were performed at Penn State University's Gear Research Institute.

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The Propulsion Environmental Working Group (PEWG) Influences Environmental Operations & Compliance Strategies At Industrial Sources & Federal Facilities

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The PEWG influences environmental operations and compliance strategies by implementing pollution prevention (P2) initiatives at federal facilities and coordinating similar efforts at industrial sources. It sets an example for government and industry cooperation by exploiting opportunities to achieve environmental excellence in the manufacturing, maintenance and rework of gas turbine engine (GTE) propulsion systems. PEWG industry members include environmental executives and material process engineers from major engine manufacturers (GE Aircraft Engines, Honeywell Engine & Services, Pratt & Whitney, Rolls-Royce Corporation, and Williams International). Military members include acquisition and logistics representatives of Army and Air Force Material Commands, Naval Air and Sea Systems Commands, and the Defense Contract Management Agency (DCMA).

Main activities of the PEWG involve exchange of information about "green" technology advances, joint assessments of environmental issues and technology opportunities, and execution of joint projects to demonstrate and validate environmentally superior materials and/or process technologies. The resources to carry out these activities are contributed by the participating members. The focus of the PEWG joint projects is to take technologies and apply them to solve issues of common environmental and readiness concerns. The PEWG currently has 14 projects ongoing for FY01. The PEWG strives to carefully balance internal and external technology resources and voluntary and contracted effort to obtain maximum value. It is positioned to promote environmental initiatives faster, cheaper and with a better technology because of leveraged activities engaging the majority of the military propulsion community. The forte of the PEWG is the introduction of cleaner materials and processes everywhere in the propulsion industrial base in one fell swoop. This paper will discuss the PEWG and how it works, and give an overview of current and future projects.

Paper not available

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Hydrogen Embrittlement in Coating Technology – Measurement & Testing

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Pre-treatment and electroplating of especially low alloyed high tensile strength steel components (such as those used in the aircraft industry) can be followed by a delayed hydrogen-induced fracture known as hydrogen embrittlement. The entire coating process has to be controlled to avoid any failure. As estimated by the fracture behaviour of differently prepared samples using a special constant load test, atomic hydrogen being evolved during the coating process and penetrating into the base metals is mainly trapped close to the interface base metal-coating. During a baking procedure after plating the atomic hydrogen can be removed from the traps and effuse through the coating as well as being more homogeneously distributed in the bulk of the base metal, both reducing the risk of embrittlement. This effect seems to be evident by tensile tests (sustained load tests and incremental step load tests) but up to now there has been no analytical proof.

Now investigations using the glow discharge emission optical spectroscopy (GD-OES) show that the hydrogen distribution in the coating, at the interface and within the bulk material, can be directly measured. The results give an improved knowledge and enable one to work out process parameters and test procedures for coating techniques to be more effective to avoid hydrogen embrittlement.

1. Introduction

Electrochemical pre-treatment and plating processes of especially low-alloyed high-strength steels (such as those used in the aircraft industry) can be followed by hydrogen embrittlement. However almost every known industry is concerned as at least some, if not a substantial quality of susceptible parts as fasteners cams, pins, rivets, springs are used everywhere. Hydrogen embrittlement occurs at the atomic level, within a metallic material. Therefore, there are no visible, exterior signs of potential failure of a part, product, or structure. The consequences are much more devastating than corrosion because failures are unexpected, occurring with no warning as the crack initiates at the atomic level, within the metal, below the surface (area of three plastic deformation). dimensional whereas corrosion occurs on the surface of the metal and can be visually detected.

2. State of the Art

Controlling hydrogen embrittlement is technically challenging because of the requirement of trying to measure the interaction of the smallest atom in the periodic table, hydrogen, on an atomic level within metals. Besides the concentration of atomic hydrogen the metal structure and strength as well as the tensile stresses (residual and applied) are the most important parameters. Classically, timeto-failure sustained load tests are conducted to evaluate the threshold stress of a component, above which the delayed fracture will occur and below which fracture will never occur. A new test method to measure the threshold stress in an accelerated, economical and quantitative way has been developed applying the Incremental Step Loading technique⁽¹⁾.

In recent investigations⁽²⁾ high strength fuse holder rings where conventionally semi-bright zinc plated, heat treated and mounted on a cylindrical pin that way, that the stress was close to the yield point but below any plastic deformation. The fracture behaviour, depending on the post-plating heat treatment after a two-month testing time is shown in Figure 1. Each point in the diagram represents the behaviour of 100 samples and therefore fulfils statistical demands. The fracture rate first increases with bake-out time, up to a maximum and finally approaches zero with further increasing time. The



Fig. 1- Fracture rate of Zn-plated fuse holder rings with respect to the annealing time at $220^{\circ}C$

reason for that behaviour is supposed to be an absorption-diffusion mechanism of hydrogen for bright or semi-bright zinc coatings⁽³⁾. According to electrochemical hydrogen permeation hydrogen concentration measurements and measurements using the hot extraction technique, a large amount of hydrogen is trapped in the zinc coating area. It is supposed that the distribution is uniform however. not and the highest concentration should be close to the zinc-base metal interface. With increasing temperature exceeding the trap energy, hydrogen diffuses mainly into the base metal as the zinc itself forms an efficient diffusion barrier. As expected this follows in a dramatical increasing of the fracture rate up to unity. With increasing bake-out time, however, a new equilibrium is read where, due to effusion and diffusion effects the hydrogen content in the base metal falls below the local critical concentration and no embrittlement occurs further on. Up to now however no analytical proof for this reasonable interpretation of the tensile test experiments has been given. Now, as efficient Glow Discharge Optical Emission Spectroscopy (GD-OES) is available, hydrogen distribution in metals and profiles can be measured.

3. Experimental Results

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The analyse of samples containing gases can be considered as one of the problematic affects in the solid sample analysis. As far as hydrogen detection is concerned especially GD-OES and Nuclear Reaction Analysis (NRA) are the very few analytical techniques capable to deal with. In the first case, the sample is sputtered using Argon ions from a low pressure plasma, where, emit light. The second method uses the principle of resonance depth profiling, the resonance reaction ${}^{1}\text{H}({}^{15}\text{N}, \alpha\gamma){}^{12}\text{C}$ being able to be used for monitoring the spatial distribution of hydrogen in material, however up to 1-2 µm in depth. Easier, cost effective and designed especially for depth profiling of thick layers (such as Zn coatings in the range of several µm thickness), GD-OES constitutes a powerful tool for hydrogen analysis in metals. Figure 2 shows the experimental setup.



Fig. 2 - The Grimm-type GD-OES source and the UV-VIS polychromator, as the commercial LECO SDP-750 spectrometer

The glow discharge is optically analysed by an UV-VIS polychromator, where the characteristic H_{α} -line of the Lyman series ($\lambda = 121.5$ nm) is detected by a photomultiplier tube. A commercial surface depth profile GD-OES instrument LECO SDP-750 (LECO Technik GmbH, Munich, Germany) was used with a Grimm-type glow discharge source (GDS) having a 2.5 mm anode diameter for the investigations⁽⁴⁾. The hydrogen detection limit is 1 ppm. It should be mentioned that in conventional GD-OES a problem with hydrogen arises as contaminations in the GDS such as residual moisture, hydrocarbures from conventional oil pumps, leak, etc. generates hydrogen which affects considerably the spectral and other properties of the GDS and the sputter rate resulting in a modified crater profile. Extensive studies dedicated to the control of the contamination have been performed in our laboratory and corrections already are implemented. Similar alterations can be observed independent of the H-source as e.g. for the spectra of TiH₂ as a sample or Ti using an argon glow discharge containing small quantifies of hydrogen⁽⁴⁾. Obviously in both cases of hydrogen

origin, a dissociation process of the molecular hydrogen takes place.

The hydrogen depth profile of a Zn-plated sample



using a commercial semi-bright low acid electrolyte is represented in Figure 3.

Fig. 3 - Depth profiling of an electrolytically deposited Znlayer

Following the profile of Zn and Fe it can be concluded that a high and constant hydrogen content is detected within the Zn layer and no significant hydrogen is present in the base metal. Obviously hydrogen is incorporated into the layer, probably as $Zn(OH)_2$ and organic additive derivates respectively. For comparison the Figures 4 and 5 show the depth profile of a Zn layer produced by hot dip galvanizing and a bulk zinc sample, both not containing a remarkable hydrogen concentration.



Fig. 4 - Depth profiling of a Zinc layer deposited by hot dip galvanising



Fig. 5 - Depth profiling of a bulk Zn-sample

A further example is given for a CoPtW-layer electrolytically deposited on a copper substrat. Figure 6a shows that GD-OES depth profiling results in a remarkable hydrogen content within the coating. No hydrogen can be found in the copper base metal, which is known to form a very efficient diffusion barrier for hydrogen. After annealing the sample at 400°C for 24 h (Figure 6b) no hydrogen can be detected any more, indicating its vanishing due to an effusion process.



Fig. 6 - Depth profiling of an electrolytically deposited CoPt-layer as plated (a) and after annealing (b)



Fig. 7 – Depth profiles of electrolitically deposited Zn layer: (i) unannealed (black curve) and (ii) annealed (red curve) 24 h, $220^{\circ}C$ in Argon.

Depth profiling of samples being annealed for 24 hours in an argon atmosphere at 220°C (Figure 7) gives evidence that the hydrogen chemically bound in the layer itself is not influenced. Further on hydrogen being trapped in the layer-base metal interface diffuses and effuses resulting in a lower concentration and more homogeneous distribution base metal. Thus following in the the interpretation of the results of sustained load test experiments.

4. Conclusions

Depth profiling of hydrogen of electrolytically deposited Zn layers confirm the diffusion/effusion model based on sustained load fracture tests. This is supporting the procedure, that the zinc plating process of especially high strength material can be controlled with respect to hydrogen embrittlement by co-plating sensible samples such as fuse holder rings and testing them in a sustained load fracture The advantage of this cost-effective test. procedure is that the plating process of every batch necessary can be monitored and documented even with respect to statistical demands.

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Status Report on Non-line-of-sight (NLOS) Hard Chromium Alternatives

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For nearly three years, CTC has been working with the U.S. Air Force Research Laboratory through the National Defense Center for Environmental Excellence (NDCEE) to evaluate electrochemical alternatives to hexavalent chromium electroplating for non-line-of-sight (NLOS) applications. In previous papers, the selection methods were described and the selected alternatives were identified. Specifically, a variety of nickel-based alloys and composition coatings were selected for testing. Since the last paper (presented at the 2001 AESF/EPA Conference in January), some of the initial screening tests have been conducted and data generated to analyze the alternative chemistries. This paper provides an update on the demonstration activities being performed, the resulting screening tests, and any conclusions that may be made.

Paper not available

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ACID CLEANING OF AIRPLANE FUSELAGE PRIOR TO PAINTING

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The current process for deoxidizing the airplane fuselage prior to painting involves power abrading with red ScotchbriteTM pads. This mechanical process is very labor intensive and may lead to musculoskeletal injuries, such as carpal tunnel syndrome. Acid cleaners/etchants were investigated to replace power abrading based on several airlines' use of acid etchants to prepare airplanes for repaint. Extensive laboratory tests were conducted with the preferred acid cleaner candidate followed by non-production trials on large panels/body sections and a one-year extended production trial in the 747 paint hangar.

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Introduction

The Everett, Renton, and North Boeing Field paint hangars have power abraded with red Scotchbrite[™] pads to mechanically deoxidize the fuselage surface prior to painting since 1970. Acceptable water-break-free surfaces and paint adhesion have resulted. However, the power abrading process is very labor intensive and may lead to musculoskeletal injuries, such as carpal tunnel syndrome. Acid cleaners/etchants were investigated to replace power abrading based on several airlines' use of acid etchants to prepare airplanes for repaint. This chemical process is ergonomically better, may reduce cycle time, and is potentially more effective in terms of uniform paint adhesion on rivets and fasteners.

Background

The Boeing paint hangar process is outlined in figure 1. Initially the airplane rolls into the paint hangar with a green temporary protective coating (TPC) covering the fuselage surface. At this point, painted surfaces which will be repainted in the hangar are sanded. The TPC remover is then applied to a wet film thickness (WFT) of

approximately 20 mils. After the TPC remover dwells on the surface for about ten (10) minutes, it is pressure rinsed off with water (<140 °F). The next step involves solvent cleaning with methyl propyl ketone/methyl ethyl ketone (MPK/MEK) (70/30) and either red ScotchbriteTM pads (Everett) or cheesecloth (Renton/North Boeing Field). Contaminants such as sealant splatter and TPC residue are removed during solvent cleaning. After solvent cleaning, the fuselage surface is power abraded using Type A, very fine ScotchbriteTM pads. The aluminum surface and pads are initially wetted prior to removing any final contamination and part of the aluminum oxide layer. Typically Boeing Quality Assurance and/or airline customers inspect for a water-break-free surface after the power abrade step. Finally, AlodineTM 1000L conversion coating is sprayed on the surface. This solution (30–40 volume percent) is allowed to remain wet on the fuselage surface for three (3) to seven (7) minutes before thorough water rinsing. The conversion coating enhances corrosion protection and paint adhesion. After drying the surface, the airplane is primed and topcoated.



Laboratory Tests

Screening tests were conducted on eleven acid cleaners/etchants. Four acid solutions did very well on all the paint adhesion tests (dry/wet tape, condensing humidity, filiform corrosion, rain erosion). However, acid cleaner D1 was the optimum candidate based on the following advantages over the other three acid etchants: (1) no fluoride which is preferable from a health/safety standpoint, (2) negligible etch rate on clad aluminum, and (3) minimal attack on K-coded titanium fasteners. The only drawback to acid cleaner D1 was its low ranking on the 4130 steel weight loss test (least critical). Fifty (50) percent by volume was chosen as the optimum concentration for acid cleaner D1/D2 (D2 is non-dyed version of D1) based on excellent clingability and a uniform coating for the entire fifteen minute dwell time. As a result, all subsequent lab tests were conducted at 50 percent concentration. Airplane compatibility (tests 1–15), equipment/waste treatment compatibility (tests 16–18), and corrosion/adhesion performance (tests 19–21) were investigated. Acid cleaner D1/D2 satisfied all test criteria except for the titanium stress corrosion cracking and hydrogen embrittlement requirements (see table 1). In addition, the following techniques were used to characterize the skin quality clad aluminum and rivet/fastener surfaces at different stages in the paint hangar process: (1) FTIR, (2) TOF-SIMS, and (3) ESCA/SEM.

	Table 1			
Acid Cleaner D1/D2 Lab Test Results				
	Test	Result		
1.	Sandwich Corrosion	Pass		
2.	Acrylic Crazing	Pass		
3.	Ti Stress	Fail		
	Corrosion Cracking			
4.	Hydrogen Embrittlement	Fail		
5.	Sealant Degradation	Pass		
6.	Rubber Degradation	Pass		
7.	Rubber	Pass		
	Discoloration/Leaching			
8.	Etch Rate	Pass		
9.	Anodized Surface	Pass		
	Weight Loss			
10.	Rivet/Fastener	Pass		
	Weight Loss			
11.	Cd Plate Removal	Pass		
12.	Gloss/Specularity	Pass		
13.	TPC Removal	Pass/Fail		
14.	Appearance	Pass		
15.	Paint Softening	Pass/Fail		
16.	Tape/Paper Compatibility	Pass		
17.	Equipment Compatibility	Maintenance		
18.	Waste Treatment Plant Compatibility	Pass		
19.	Alodine 1000 Coating Weight	Pass		
20.	Alodine 1000 Salt Spray	Pass		
21.	Paint Adhesion	Pass		

Conclusions

- The acid cleaner D1/D2 process is equivalent to the power abrade process in terms of skin and rivet/fastener paint adhesion. The optimum parameters for the acid cleaner process are 50 percent concentration and a 10-20 minute contact time. Alodine[™] 1000L conversion coating is required in combination with acid cleaner D1/D2 in order to achieve adequate paint adhesion.
- 2. The test panels from the acid cleaner D1/D2 process were generally as clean as the ones that were power abraded based on Fourier Transform Infrared Spectroscopy (FTIR) analysis (figure 2). The small number of samples are simply an indication of the true results, and many more panels would have to be tested to prove that acid cleaning was more effective than power abrading.
- 3. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) analysis revealed no TPC or acid cleaner D1 residue on a skin quality clad aluminum surface after a 15 minute D1 contact time and water rinsing. However, possible reaction by-products in the form of aromatic hydrocarbon species were detected (figure 3).
- 4. One possible theory on why the oxide thickness of aluminum stayed relatively constant (180 Å) after acid cleaning with solution D1 is that D1 initially <u>dissolves</u>(-) the oxide layer and then <u>forms</u>(+) a thin reaction layer as an adhesion promoter (table 2).



Figure 2 -The C-H Stretch Region of all Nine Aluminum Test Panels (Gold Background)



Figure 3 -Positive TOF-SIMS Spectrum of Panel #17 (D1-15 Minutes)

Table 2 Oxide Thickness Values from ESCA Sputter Profiles					
Panel No.	Treatment	<u>Oxide Thickness (Å)</u>			
0	As Received	165			
18	TPC Removal	200			
19	MEK	190			
20	Power Abrade	260			
22	D1 (15 minutes)	180			
23	Power Abrade + Alodine 1000L	315			
25	D1 (15 minutes) + Alodine 1000L	185			

Formulation and Evaluation of Chemistries for Cleaning Applications

By Rick Reynolds, DuPont Chemical Solutions Enterprise

In today's accelerated regulatory environment, new cleaning chemistries and formulations are introduced to the market at a sometimes-alarming rate. As such, companies face the common challenge of adequate and cost effective performance evaluation. The purpose of this paper is to introduce methods by which those who use chemicals can increase their selection efficiency, minimizing the time and effort to do screenings, and maximize the quality of the results of those screenings. The session will provide insight on future regulatory trends and keys to ensuring compliance. Simple, practical methods will be presented by which anyone can effectively conduct performance screenings for making concrete decisions about alternative cleaning agent selection.

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Introduction

Welcome to 2001. Over 12 years after the mad dash to replace chemicals brought on by Montreal Protocol, cleaning processes for manufacturing, repair, and maintenance have evolved significantly. Over 99% of companies have fully made the transition from ozone-depleting compounds. A few still remain, especially government facilities and government contractors, who use chemicals from stockpiles due to inability to locate adequate replacements to clean critical parts. This population, however, is quickly declining as a function of both reasonable replacements being identified and the added pressure of dwindling stockpiles

Today's regulatory environment is constantly changing, becoming more and more restrictive with each passing day. In addition, the first generation of cleaning chemistry replacements offered far less than "drop-in" replacements. Performance was not always equal and each chemical came with a host of new baggage like VOCs, toxicity, waste concerns, etc. There is a strong desire to reduce this baggage, coupled with consistent advances in cleaning chemistry from the multitude of vendors offering so-called "ideal" solutions to all of cleaning's problems. A good analogy would be to say that there is no "Microsoft" when it comes to cleaning chemicals. This definitely has its pros and cons, and depending on whom you ask, opinions vary widely. One of its primary effects, however, is to add both end-user confusion in choosing a reliable product and significantly increasing the number of candidate solutions one must evaluate.

This confusion and frustration is brought to an even higher level when faced with the challenge of quickly, fairly, and effectively testing potential replacements. The quality and frequency with which this testing is performed is critical. It has a strong and direct impact on ensuring that the cleaning process produces both top quality results that maximize revenues and a safety profile that minimizes resource expenditures.

The purpose of this paper is to introduce methods by which those who use cleaning agents can increase their selection efficiency, minimize the time and effort to do screenings, and maximize the quality of the results of those screenings. This can occur by following a diligent process of both carefully researching potential solutions first and then a scientific approach to the screening process.

The Scientific Method

Any evaluation of new candidates is technically an experiment and as such, should be done by employing good science. Critical to ensuring that any experiment is performed properly, the scientific method is a rigorous process that employs four simple steps:

- 1. Observation
- 2. Hypothesis
- 3. Prediction
- 4. Testing

Notice that testing comes last. This is because without doing the right work prior to testing, those tests essentially become meaningless, as the experimenter may not know what the tests are really saying. A good example of this would be the performance seen by using a replacement solvent at a higher temperature. Did the solvent work because it was a better solvent or because the heat was higher? Would the old solvent have worked just as well at this temperature? Was the real problem not the chemical at all, but some mechanical deficiency?

To many, this process may just seem like common sense, and for those experienced in the process, it is. Understanding each step and its place in the solution process, however, is key to ensuring that solid and reliable results are obtained each time the process is initiated. Lets discuss each of the steps in the scientific method and relate them to evaluating new chemistries.

Observation: Good scientists are observant and notice everything about a given situation. For example in a given cleaning situation, it is important to recognize and record everything that may influence the process, of which, chemistry is just one element. Other important elements include mechanical action (spraying, pressure, wiping, etc), temperature, equipment function, soil load and type, cleaning time, etc. The key to the observation step is to feel confident that the chemistry is what needs to be replaced prior to embarking on a process to do so. If the key reason for replacement is not performance related (i.e.: toxicity, treatability, etc.), this step might seem unnecessary, however, knowing all of this information will be critical when determining the performance of a new compound.

An example of an observation would be that particles are being left behind from a wipe cleaning application. This in effect becomes the problem that needs to be solved. The next step in the scientific method describes how to handle that observation.

Hypothesis: This is a tentative explanation for what is being observed, not an actual observation. It is a good chance for the experimenter's past experiences with similar problems to assist in making the most accurate solution to the observation requiring action. It is important to propose as many hypotheses as possible and be sure that both deductive reasoning and experimentation can test them.

Two good example of hypotheses could be drawn from this given wipe-cleaning situation where particulate soil is being registered in cleaning verifications. One hypothesis would be that the cleaning agent is not doing an effective job of removing the particulates. Another would be that these particles are being shed from the wipe substrate. Both hypotheses can be tested through proper experimental design.

Prediction: This is the point where the experimenter uses deductive reasoning to test the hypothesis he has proposed. In other words, one "predicts" that specific results will be seen if something is tested. For example, one might predict that if the wipe substrate were causing the particulates, then using a non-linting wipe would correct the problem. If the problem lies in the cleaning agent, however, one would predict that a better cleaning agent will be the solution.

Testing: This is the final step in the scientific method where all of the due diligence put forth in prior steps comes together to determine if a solution can be found. The most important key to testing is to run "controlled" experiments. Experimenters must contrast experimental groups with a "control" group, which represents the current application being replaced. The two groups must be treated exactly equal except for the one variable being tested. For example, when testing a new wipe substrate, it is key to ensure that the exact same chemistry is used and that the temperature, pressure, and number of wipe cycles are identical in both tests. The only difference can be the substrate

Also, when running experiments, it is critical to do replication of tests. Every test should be replicated at least 3 times to ensure that the results are true and minimize the occurrence of anomalies that would not show up in real life cleaning.

Finally, the researcher must be able to extract quantitative data from the tests. Just saying that Prototype B works better than Prototype A will not do. Unless the degree of improvement can be measured in some fashion, the justification for making a switch could be questionable. Much of this can be resolved just by using a set of predetermined standards. Then, results can be compared to standards that represent "pass or fail" results.

That concludes the discussion of following the scientific method when evaluating new options for cleaning. Though general and possibly very simplistic in nature, it represents a proven reliable method of doing the right research to obtain sustainable and credible results. It is now prudent to move into a more targeted discussion of steps to follow when working with cleaning chemistries and evaluating new ones for use in various applications.

The following steps 1-3 would be considered things to be done in between the *prediction* and *testing* steps of the scientific method. By performing these steps properly, the researcher can intelligently narrow the candidates that should be tested as well as significantly raising the likelihood that a suitable and sustainable replacement will be identified.

Step 1: Set the priorities

It is a rare case that new chemistries are brought on site for no particular reason. It is key that the reason new compounds are being sought be set as priority number one. From there, the remaining priorities need to be set and ordered by importance. Be sure that every issue that can accompany a chemical is accounted for and noted as a "need" or a "want." For example, ozone compatibility is a "need" for 99.9% of all cleaning applications. Other needs would be non-carcinogenicity and nonflammability. Low odor or recyclability may actually just be "wants" as these issues can be managed and still produce quality parts. In most cases, chemical cost, though often touted as a "need," is in reality, just a "want." Used properly, most good chemicals incoming costs can be positively balanced against the benefits they offer. It is important to realize that in any situation, you always get what you pay for.

Step 2: Do your homework

It's a common and not necessarily wrong practice that frequently occurs in today's cleaning applications. Without spending a significant level of time researching all of the critical issues specific chemistries. associated with these chemistries are brought into facilities, quickly and haphazardly evaluated, and later, found to have flaw that makes them significantly some unattractive. From that point on, resources are put into efforts to identify the next replacement chemistry. These resources are, to a large extent, wasted because had the process been done right the first time, those resources could be spent more productively elsewhere. In addition, it can easily become an endless cycle as one chemistry after another is evaluated without maximum efficiency.

To prevent this from occurring, it is essential that all relevant qualities of a proposed solution be fully researched. Make a list of key questions to be answered; especially those that will impact the specific process being upgraded. Be sure to know which criteria <u>must</u> versus the ones that <u>should</u> be met. The following list provides a good starting point for a list of critical areas of knowledge to which answers should be provided before moving forward:

- 1. Physical properties of the chemistry
 - a. Flashpoint
 - b. Odor
 - c. Vapor Pressure
 - d. % Solids
 - e. Level of Impurities
- 2. Necessary equipment to maximize worker safety
- 3. Proper equipment and operating conditions needed to maximize performance

- 4. Incompatibilities
- 5. References of current customers
- 6. Technical service agreement

Of course there may be other key attributes that are needed depending on the application. A final hint is that if vendors are unwilling or unable to provide important data on products, those products should be avoided. There is no point risking a significant loss of time and resources because negative properties of the chemical were discovered too late and because of lack of due diligence on the part of the vendor or customer. Finally, the old adage remains that anything that looks too good to be true probably is.

Step 3: Ensure smooth production

In many cases, the stated reason for misguided decisions is that there was not enough time to do a thorough evaluation. Production needed to begin immediately and the old chemistry needed to be removed or money/opportunity would be lost. While this is certainly an easily understandable scenario, the money and opportunity gained in the short term rarely outweighs that which is lost in the long term. Most of this urgency is caused by two thing that act together or alone:

1. Someone waited until the last minute to evaluate replacements - No explanation on remedies needed here.

2. Any worthwhile testing is performed on the actual production line rather than a "proving area" due to the lack of effective and correlatable test methods. Many are all too familiar with the feeling of "it doesn't work right until it works on the real thing."

It therefore becomes essential to complete the following steps before actually disturbing production:

1. Begin researching replacements immediately

2. Set up a method for gauging performance that correlates with production, but does not require shutdown for testing; in other words, a reliable "lab test."

3. Use that method to narrow candidates down to one or two before testing on the production line.

Step 4: The methods

Evaluating the performance of different chemicals can be a very ambiguous and misleading science if not performed correctly and with the right perspective on the data. This is exceedingly true in the case of solvent versus aqueous chemistries. In most cases, solvents work primarily by dissolving soils into them. Aqueous chemistries, however, generally need some form of mechanical action in order to effectively activate their cleaning powers. Just to name a few, wetting, emulsification, dispersion, and suspension can only be fully optimized with some sort of mixing and impingement.

Since almost all cleaning systems work using a variable mixture of chemical and mechanical factors, it is critical to isolate each factor and note its impact on cleaning. By doing so, it will be possible to theorize what ideal combination of potential variables will be needed to do the most effective job of cleaning. For example, if very delicate parts are being cleaned, then strong mechanical force is impossible. As such, pure chemical factors take a higher seat in the order of importance. A solvent may be the ideal choice. On the other hand, where parts are rugged, but flammability and vapors may be an issue, pure chemical effects are less needed and can be replaced by aqueous chemistries coupled with stronger impingement.

In lab-scale evaluations, there are three key steps in testing: sample preparation, testing, and results analysis. Each step is equally critical and defects in any one can result in erroneous evaluations.

Sample preparation is the first step in conducting any lab scale evaluation. How one prepares samples for testing is just as critical as how the tests themselves are run. Any error or improper variability in sample preparation will ultimately lead to invalid test results. Any improvements or shortcomings exhibited by tests can then potentially be traced to variability in sample prep rather than strengths or weaknesses of the solutions.

For each of the tests in this paper, sample preparation is identical except that the size of the test coupon varies by test and will be noted in the procedure. In general test coupons are prepared by placing a known and repeatable weight of "soil" (ie: grease, oil) onto the coupon. The test coupon should be made from a material equal or similar to that which will be used in production. It is critical that the coupon material not be significantly different (ie: metal vs. plastic vs. glass). This is because each material has a specific critical surface tension that can have a direct impact on the ease with which soils are removed. A final note on sample preparation is to ensure that both the environment in which samples are prepared and the length of time before they are tested stays constant.

To accomplish the task of properly evaluating chemistries, three basic and variable "lab tests" can be constructed. Each test can be set up to minimize and maximize both chemical and mechanical factors in cleaning. When used together, the combined data can be extremely telling as to how cleaning will be accomplished in a production best scale Figure 1 shows a graphic environment. representation of the stress that each test can place on both mechanical and chemical properties. This gives the experimenter an idea what test(s) to use and in what manner in order to most accurately evaluate solutions, as they would be used in production.

Chemical		Mechanical
1	2	3

The following discusses these three tests and how each can be custom tailored to give data that corresponds to varying blends of chemical and mechanical factors. Always remember to follow safe procedures based on the chemicals in use. Medium to high vapor pressure solvents should be used in a hood or well-ventilated area.

Test #1: Immersion – This is a test based primarily on chemical factors and incorporates varying levels of mechanical factors. The immersion test is an ideal test for pure solvency and showing the effects that chemicals have in both static and agitated conditions under liquid. Temperature can be varied from ambient through super-heated. Agitation can be varied from zero agitation to intense agitation. With this test, the effects of pure solvency can be explored as well as how that solvency can be enhanced with agitation. It also shows how a good cleaning agent can remove and emulsify or split soils given the proper conditions. On a one to one basis, this is a good test for mimicking what happens in a vapor degreaser or agitated/non-agitated dip tank.

Appendix A shows a diagram of the system as well as the items needed in order to make it function properly. It is important to remember to run all prototypes at the same soil weight, time interval, temperature, and RPM so as not to void results with a second variable.

Test #2: Impingement – This test now incorporates the impingement factor which can be correlated to any spraying or pouring action in a cleaning process. This is an ideal way to look at comparing a solvent versus and aqueous agent. It allows a cleaning agent to exhibit its qualities as a solvent and its qualities for wetting, soil rollup, emulsification, and dispersion all in one tunable step.

The temperature of the solution in the system can be varied, but always check the temperature at the point of impingement as heat exchange will occur in the downspout. Also, the height and angle of impingement will have a significant impact on cleaning. The sharper the angle of impact, and the higher the liquid drop, the easier cleaning will occur. Try to adjust parameters to most closely mimic what parts will actually see.

Appendix B shows a diagram of the system as well as the items needed in order to make it function properly. Again, it is important to remember to run all prototypes at the same soil weight, time interval, temperature, and height/angle of impingement so as not to void results with a second variable.

Test #3: Wiping – This test has the best potential for looking at purely mechanical effects coupled with the increased efficiency brought in by the right solvent. Not only is it the ideal test to use when evaluating wipes, but it also gives an outstanding indication of a soil's ability to be removed by purely mechanical forces.

Variables include the quality and type of wipe substrate, which can make a huge impact on the efficiency of the product. The obvious one is the cleaning agent on the wipe, however, level of cleaning agent, pressure, and number of cycles can all have a huge impact on performance. Appendix C shows a diagram of the system as well as the items needed in order to make it function properly. As always, it is important to remember to run all prototypes with the same soil weight, number of cycles, substrate, and pressure so as not to void results with a second variable.

Proper analysis of the data collected in testing is critical to ensure that the results are presented in a manner that shows exactly how well or poorly each cleaning agent performed under the conditions of the test. Although there are a number of methods by which analysis can occur (i.e. particle counting, Millipore test, non-volatile residue, weight difference, contact angle, etc.) the key is to be consistent with analysis method.

Remember that these tests are not the actual cleaning system to be used in real life. As such, they should not be expected to give production quality results and should therefore not be analyzed with the same scrutiny. Rather, the experimenter needs to set a "standard" that represents what is currently being done in real life cleaning. If that means that the test leaves a certain level of soil behind, that's OK. In fact, it is critical to calibrate each test such that the control fails to fully clean to some extent. Otherwise, it will be impossible to determine which prototypes actually performed better. Some may even argue that this does not hold when looking for equal performance. Unfortunately, this is when the case holds most strongly. For example, if the control system fully cleans a coupon in two cycles or ten minutes, but the test runs for 4 cycles or twenty minutes, the end analysis is the same for a system that cleans worse but in three cycles or fifteen minutes. Be careful!

Finally, it is important to note that these methods are for the most part, merely correlative in nature. Aside from the wipe test, they do not represent exact mimics of real-life cleaning situations. These tests need to be properly calibrated such that either the results will directly correlate to improvements or shortcomings in the actual cleaning system or, more likely, simply give the experimenter a solid idea of the level of improvement likely to be seen in real life. Also, realize that the tests also do not account for other very critical factors in cleaning systems such as corrosion, foaming, recyclability, etc. These are critical factors for which preliminary data should be available from manufacturers that can be verified in house once cleaning results warrant further qualification.

Step 4: Do the math

How much money will implementing this system actually save? Are the benefits worth the cost? Many conventional wisdoms state that this is something that should be considered prior to testing. Unfortunately in many cleaning cases, nothing could be more misleading. It is very easy to put together a list of figures on a new system, compare them to current ones, and quickly come to the conclusion that the new system will be more expensive.

When looking at replacement options, it is crucial to evaluate what they offer from a global perspective. The term global means the company as a whole and any parties it affects such as the environment, surrounding community, and its customers. Each has an impact, direct or indirect, on the company's short term and long term profitability. Good examples of global factors not apparent in just and initial number comparison are reduced energy needed to clean, less waste, higher throughput, lower reject rate, improved part quality, and lower customer complaints.

The bottom line is that its essential to do a thorough front and back end evaluation on the economic pros and cons of any potential replacements. The upfront analysis can do a good job of determining if a proposed system is within the ballpark of what may or may not be acceptable. From there, it is imperative to consider both the performance improvements and the global benefits that will lead to lower overall costs.

Conclusion

In conclusion, it is safe to say that when evaluating potential replacements for cleaning systems, having a simple method for screening is highly valuable to the overall process. No method can be to simple, however, without detracting from the quality of the data it provides. It therefore becomes necessary to identify and implement methods which simply and speed the qualification process and do so in a high quality manner. The methods presented in this paper can be very powerful when used alone to identify trends and improvements in cleaning agents. When used and analyzed properly and together, however, they wield an enormous power to effectively separate and sort any and all cleaning agents as to their level performance alone and with varied degrees and types of mechanical synergy.

Appendix A – Immersion Test



Procedure

1. Prepare a 1" x 2" test coupon of appropriate composition by placing a known quantity of soil (about 0.5g) in the center of the coupon. When applying soil, it is sometimes useful to draw a repeatable area on the coupon by tracing a coin and placing the soil within that circle.

2. Place test solution at appropriate concentration in test vessel and heat to desired temperature. When using solvents, exercise caution by venting vapors and removing any sources of spark.

3. Set stir bar to spin at desired RPM. Obviously, more spin means more mechanical action.

4. Set the timer for the desired test time interval.

5. Clip the prepared test coupon in the hemostat and place into the test solution

- 6. When time interval is up, remove the coupon
- 7. Rinse coupon in clean solvent or water and allow to dry
- 8. Analyze residue by preferred method

<u>Materials</u>

- 1. Stir Plate
- 2. Magnetic Stir Bar
- 3. Temperature Probe
- 4. 500ml Fleaker
- 5. Sample Assembly
- 6. "Soiled" Aluminum 1100 Coupon
- 7. Hemostat
- * Materials available from Lab Supply Companies
 - Cole Parmer (800) 323-4340
 - VWR (800) 932-5000

Appendix B – Impingement Test



Procedure

1. Prepare a 1" x 2" test coupon of appropriate composition by placing a known quantity of soil (about 0.5g) in the center of the coupon. When applying soil, it is sometimes useful to draw a repeatable area on the coupon by tracing a coin and placing the soil within that circle.

2. Place test solution at appropriate concentration in aspirator bottle at desired temperature. When using solvents, exercise caution by venting vapors and removing any sources of spark.

- 3. Ensure flow outlet is in proper position
- 4. Clip the prepared test coupon into place
- 5. Open stopcock to start test
- 6. When time interval is up, remove the coupon
- 7. Rinse coupon in clean solvent or water and allow to dry
- 8. Analyze residue by preferred method

Materials

- 1. 300 ml Aspirator Bottle
- 2. Funnel
- 3. Beaker Clamp
- 4. Teflon Tubing
- 5. Stopcock
- 6. Disposable Pipet Tip
- 7. "Soiled" Aluminum 1100 Coupon Assembly
- 8. Catch Beaker
- Materials available from Lab Supply Companies
 Cole Parmer (800) 323-4340
 - VWR (800) 932-5000

Appendix C – Wipe Test



Procedure

1. Prepare a 6" x 6" test coupon of appropriate composition by placing a known quantity of soil (about 0.5g) in the center of the coupon. When applying soil, it is sometimes useful to draw a repeatable area on the coupon by tracing a coin and placing the soil within that circle.

2. Prepare substrate by folding and wetting with appropriate level of cleaning agent (about 5-6g). When using solvents, exercise caution by venting vapors and removing any sources of spark.

3. Place wetted substrate on soil with standard weight on top 4. With no additional pressure downward, move the substrate forward and backward to the edges of the tile 3 full cycles.

5. Remove substrate, refold to a clean surface, and repeat scrub.

6. Repeat cycle enough times to calibrate standard to a level below absolute clean

7. After test, rinse coupon in clean solvent or water and allow to dry

Materials

- 1. White Ceramic Tile
- 2. Black Ceramic Tile
- 3. Folded Wipe Substrate
- 4. Standard Weight
- * Materials available from Lab Supply Companies
 - Cole Parmer (800) 323-4340
 - VWR (800) 932-5000
- * Gardner Abrasion Tester
 - Byk-Gardner (800) 343-7721

8. Analyze residue by preferred method

Aircraft Engine Parts Washwater Recycling System— An EPA ETV-MF P2 Technologies Center Test Report

Donn Brown, P.E., Concurrent Technologies Corporation, Largo, FL & Dr. A. Gus Eskamani, CAMP, Inc., Cleveland, OH

The U.S. EPA Environmental Technology Verification for Metal Finishing Pollution Prevention (P2) Technologies Center conducts performance verifications of innovative, commercially ready technologies designed to improve industry performance and achieve cost-effective P2 solutions. Test plans are developed between CTC, EPA and the technology supplier. Verification testing is conducted under strict EPA guidelines in metal finishing shops under actual operating conditions. This paper will discuss the verification test results of the treatment of water used to clean aircraft engines and parts. The primary treatment process involves the use of a flocculating agent to encapsulate oil and grease as well as heavy metals. The resulting water is either recycled or further treaeted by activated carbon/ion exchange resin to make it suitable for discharge to the publicly owned treatment works (POTW).

Paper not available

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Status of DoD Program on Replacement of Hard Chrome Plating With Thermal Spray Coatings on Aircraft Components

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The U.S. Department of Defense (DoD) tri-service/industry Hard Chrome Alternatives Team (HCAT) is currently partnering with two other DoD organizations [the Joint Group on Pollution Prvention (JG-PP) and the Propulsion Environmental working Group (PEWG)] to execute projects to qualify advanced thermal spray coatings as a replacement for hard chrome plating. Because of different materials and performance requirements, the individual projects are associated with landing gear, propeller hubs, hydraulic actuators, helicopter dynamic components, and gas turbine engine components. Working with OEMs and other DoD stakeholders, Joint Test Protocols (JTP) have been or are being developed that delineate all of the materials and component testing required for the qualification and implementation of the thermal spray coatings. Results will be presented for the testing in the landing gear and propeller hub projects, and overviews of the JTPs in the other projects will be presented. Information related to development of standards and preparation of cost/benefit analyses will also be presented.

Paper not available

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The manufacturing of carbide materials for HVOF

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1. Introduction

Industries are finding new and innovative applications for thermally applied coatings. Surface treatments can now enhance the wear characteristics and life expectancies of a diverse array of parts. Generally these surface treatments must not alter the fit, form, and function of the basic part. Additionally, those surface treatments must also match or exceed the other requirements of the part and the application, e.g. surface finish, corrosion resistance, fatigue strengths, etc. With challenges such as these, each phase of the coating process becomes mission critical.

New ways of manufacturing the materials to be coated are offering industry a way to solve the problem of having one surface treatment meet all the performance requirements needed. Specifically, the formulation of composite materials that are manufactured with individual elements that when combined will fulfil the various requirements. Yet these new material solutions must also comply with the economic requirements. Coatings must be price competitive to the traditional methods being reviewed. In those instances where thermal coatings have elevated process costs, these costs may be more than offset by processing time reductions or life cycle extensions.

The HVOF process is gaining acceptance as the method of choice for line-of-sight application of dependable and cost effective surface enhancements. There are a variety of process techniques from different industry sources. The consumer can pick and choose what type of equipment would fit into their shop environment best. All the devices have the capability to apply materials of unique chemistries that may indeed achieve the required enhancement in the different modes... wear, corrosion, fatigue, etc. But no matter what the choice on equipment type or process uniqueness, they will all require a careful and proper choice in feedstock.

One group of materials with a long history of success are the carbide containing materials. The main constituents are tungsten carbide and/or chromium carbides with the addition of matrix metals, usually Ni, Co and Cr or alloys of these. The coating properties are mainly influenced by the application method technology and the feedstock powder properties. The feedstock properties are influenced by these variables; the type and selection of raw materials, the homogenizing process, the spheriodization methods, the sintering, the screen size distribution, the chemical composition, and the phase structure of the matrix metal.

This presentation will discuss and identify the manufacturing processes and discuss the relationship of these to the performance of the powder material in the application intended. Those involved in the application and/or acceptance of thermal applied coatings should gain from this information information that will allow more informed decisions relative to the selection of powders for critical coatings.

2. Raw materials

2.1 Tungsten carbide

Due to its high hardness and its high wear resistance tungsten carbide is one of the most important materials in wear resistant alloys and coatings. The stoechiometric δ -WC with a carbon content of 6,13 wt.-% and the eutectic cast tungsten carbide WC/W₂C with a carbon content of 3,8-4,1 wt.-% are of technical importance.

The stoechiometric tungsten mono carbide has a hardness of 1800-2000 Hv_{o,5}. At temperatures above 550°C it tends toward oxidation. Under standard conditions tungsten monocarbide cannot be brought to a molten condition by molten metal. Therefore it will not precipitate complex carbide phases. A loss of carbon and the origination of W_2 C-phases is required. Tungsten mono carbide decomposes into W-C molten and solid carbon at a temperature of 2785°C. It re-solidifies mainly

into eutectic WC/ W₂C with an accicular structure. This process can and does partially occur during HVOF spraying. It is more known during plasma spraying and plasma densifying, due to the higher temperatures of these processes.

Compared to tungsten mono carbide, cast tungsten carbide has higher hardness and offers the potential for improved wear resistance. Production is performed in induction furnaces at temperatures of 2785°C. The molten product is chill-cast into cooled graphite or copper mold. The quenching retains an accicular structure of precipitated WC in a W2C matrix. The cast ingots are crushed to the required size distribution by repeated crushing procedures, generally in a hammer mill. The iron elements of the mill wear during the process and an increase of iron contamination up to 1 wt.-% cannot be avoided. Therefore material manufactured by the cast and crushed method is not always suitable for application in corrosive environments. Also, the W2C phases can be decomposed by molten metals. This results in the formation of η -carbide phases and grain growth of the WC phases can occur.

The previously mentioned η -carbide phases are hard but brittle phases. They originate from tungsten, carbon, and the matrix metal (Ni,Co). They do impart additional hardening of the carbide coating, but with this comes a loss of ductility. Impact resistance as well as resistance against pressure, cavitation and fatigue are decreased. η -carbide containing coatings are also more prone to the formation of fine cracks leading through the whole coating down to the substrate. Penetration of corrosive elements to the substrate. Coating spalling and/or blistering can be the consequence. These failure modes would negatively impact the continued servicability in critical applications like hydro turbines, or aerospace turbines/components.

Generally the stoechiometric tungsten carbide is more suitable for thermal sprayed coatings. The reason is the slower interaction between WC and alloying ingredients of the matrix metals. Therefore the phase structure is more close to the selected raw material.

2.2 Chromium Carbide

Depending on the production process, chromium carbide generally exists in three different compositions, the Cr23C6 (5,45 wt.-% C), the Cr7C3 (9 wt.-% C) and the Cr3C2 (13,33 wt.-%). Most common for thermal spraying interest is the Cr3C2. This chromium carbide has the highest hardness and wear resistance. The production process and the raw material used can introduce impurities, e.g. sulfur or iron. Depending on the application, especially in corrosive environments, it is often necessary to keep these contaminations below a strict limit.

Chromium carbide can be exposed to oxygen up to a temperature of 850°C without oxidation. Therefore it is used for coatings in high temperature applications >500°C. The specific density of Cr3C2 (6,68 g/cc) is lower compared to the specific density of tungsten carbide (15,72 g/cc). The melting point is 1895°C.

2.3 Matrix materials

Matrix metal alloys were successfully developed in the cemented carbide industry and the welding industry and have been successfully transferred into the thermal spraying by use of composite carbide materials. Pure metals such as nickel and cobalt are used as well as alloys. Two typical alloys are cobalt-chromium (70/30) and nickel-chromium (80/20). The ingredients of multi metal alloys are added to the mixing process in element form. The alloying process occurs during the sintering phase. Therefore the metals have to be oxygen free as oxidation during the manufacturing process can prevent the alloying during the sintering. The oxygen shells act as diffusion barriers. If high oxygen levels are present in the manufacturing process, the incompletely alloyed metal matrix materials will not exhibit the same desired properties as if the alloying were complete. Problems could occur during spraying. For example, CrC-NiCr coatings can form dark layers of chromium oxide. The formation of these dark areas is accelerated by chromium rich areas in the powder. If the coating is to be used in a high temperature application, the nickel rich areas may become susceptible to the attack of sulfur. Each application requires unique quality of alloyed matrices. The use of a pre-alloyed matrix material is not viable due to cost. The materials would be required in

1µm nominal size that is prohibitively expensive to produce and procure.

2.4 Grain size of raw materials

Experience gained from the cemented carbide industry has shown that the grain size of the starting raw materials is of high importance. Depending on the homogenisation process the tungsten carbides could be milled down, but this is not possible with the metallic ingredients due to their ductility. They should be in a range of 1-2µm as a raw material to ensure a complete alloying. The alloying is dependant on a diffusion mechanism. If the metal particles are too coarse, they cannot be alloyed completely. Again, any metal rich areas decrease the wear resistance. The coating would also exhibit non-uniformity in respect to hardness values.

The selection of the optimum carbide size is of extreme importance. The more homogeneous the carbide sizes are the better and more uniform the coating properties can be expected. Therefore, the raw materials should have a narrow distribution prior to inclusion in the manufacturing process. Milling during the homogenizing process should be avoided as to not alter the expected carbide distribution. The required size distribution for the tungsten carbides has to be adapted to the application. As in the cemented carbide production carbide sizes of 0.6μ m, 0.8μ m, 1μ m, 3μ m and 5μ m are common. It is necessary that all carbides be within a certain specification. The chromium carbides should be in a range below 5μ m to avoid a decrease of the deposition efficiency.

3. The homogenizing process

The selected raw materials must be completely and thoroughly distributed through out the production lot before the spraydrying portion of the manufacturing process can be performed. There are different approaches utilized to accomplish this mandatory and critical step.

3.1 Ball Milling

Ball mills are generally horizontal arranged chambers filled with iron or cemented carbide balls. The ball milling process is a dry milling process without any liquids. Depending on the following manufacturing process the raw materials are blended together with an organic binder such as paraffin or PVA. The mixing time and the ball diameter can be altered depending on the type and ratio of the starting materials. Due to the high energy input and the oxygen atmosphere an increase in the oxygen content level cannot be avoided in the standard dry ball milling process. If iron balls are utilized, they will wear similar to the hammer mill elements and impart contamination of the material with abraded iron. The quality of the homogenizing process is depends on the following primary factors; milling time, ball/powder relation, ball diameter, and rotation speed of the chamber.

3.2 Attritor milling

Attritors are special vertical ball mills. They are usually filled with cemented carbides and an σganic solvent. The liquid film between the balls and the strictly controlled ball diameters prevent size changes of the base materials. Therefore the carbide size in the finished powder can be tailored by the right choice of the carbide size in the raw material at the beginning of the production process. This allows for a much more controlled and repeatable production method. Attritor milling is the "state of the art" in the cemented carbide manufacturing.

3.3 Dry blending

An old fashion way for homogenizing the starting materials is dry blending. For this process tumbler blender or ball mills without balls are used. There is no forced incorporation of the materials in the dry blending process and the level of homogenizing is truly limited.

4. Manufacturing processes

To produce sprayable granulates out of the pre-blended raw materials a few manufacturing steps are necessary. The blends have to be prepared for the sintering process. A general distinction is made between the "sinter and crushing"-process and the agglomeration and sintering.

4.1 Compressing

For the "sinter and crushing"-process the blended raw materials are pressed into bricks or cylinders. A pressing aid is used to improve degree of compaction. The size of the brick or cylinders must be limited to ensure a homogeneous sintering through the whole block.

4.2 Spray drying in a water based system

For the spray drying in a water based system the homogenized starting materials are mixed bgether with water soluble binder (glue) and water. The solution is atomised in the spraying chamber either by a lance/nozzle system or a centrifugal impellor style atomizer. Small water drops carrying the solid raw materials are formed. Once exposed to the elevated temperature of the drying chamber the water quickly evaporates in the hot air/water steam atmosphere. The formed micro pellets are held together by the organic binder and the dried shell of the particle. Drying chamber temperature of 180-210°C inlet and 125-135°C outlet are typical.

Spraydrying has the advantage to produce spherical micropellets with a uniform shape. These agglomerates are formed out of a multitude of fine distributed powder particles. The use of an open circuit system with an air/water steam atmosphere has the disadvantage of producing hollow and porous particles. These hollow and porous particles will often fracture into irregular shaped morphologies during later production process phases. Also, since the drying chamber is a oxygen and moisture rich environment, the oxidation of the matrix metals cannot be avoided. For the production of multi metal matrices such as Co-Cr or Ni-Cr this oxidation level can become a significant detriment to the process. The oxide skin on the metallic particles acts as a diffusion barrier and prevents the alloying process during the sintering. The consequences of not completely alloyed powders are manifested as a non-uniformity in the corrosion resistance of the coating or dark chromium oxide layers in a CrC-NiCr coating.

4.3 Spray drying in a closed loop system

In contrast to the spray drying in an open loop system alcohol is used as a solvent in a closed loop system. The atmosphere is an inert gas with an oxygen content below 0.2 wt.-%. The homogenized starting materials are mixed together with the alcohol and an organic binder during attritor milling process step. Actual atomising is comparable to the one in an open loop system.

Standard inlet temperatures for the gas are 90-110°C. The outlet temperatures are approximately 65-70°C. This low temperature level ensures a soft evaporation of the solvent without developing a hard skin or the origination of hollow particles. The advantage of this system is to make possible the production of very dense micro pellets with a typical oxygen content of 150-300 ppm. This oxygen content is comparable to the oxygen content of gas atomised metal powders. Due to the preparing attritor milling the carbide grain sizes can be controlled in a narrow range.

5. Sintering

The first sintering step is the binder evaporation phase where the organic binder is removed. This phase is critical because the consequence of a too slow evaporation would be a deformation of the micro pellets. A too fast driven evaporation could crack the organic binder and contaminate the material with carbon or alkali metals.

For the sintering process different types of furnaces can be used. Generally temperatures are between 1100°C and 1400°C. The temperature and the sintering time influence the cohesion between the carbides and the metallic particles. Too low sintered powders tend to burst or crack when they are injected in the nozzle or the burning chamber. The result in HVOF is nozzle clogging. Too high sintered powders cannot be sufficiently softened during the spraying process. Internal porosity in the coating and low deposition efficiency are the consequence of too high a sintering level.

5.1 Hydrogen push/pull furnace

The "old fashion" way for the sintering is by use of hydrogen push/pull furnaces. They are a series of heating chambers arranged in series. The product to be sintered is loaded into carbon crucibles, or boats, and then drawn through the furnace. The sintering cycle is dependant on the temperature and size of the separate chamber areas, and the speed at which the product is moved through the furnace. Original furnaces of this type are generally considered low-tech and are indeed very labor intensive. Through-put is dependant on dedicated manpower to load and unload during any and all times the furnace is operating.

Hydrogen furnaces have the advantage of a reducing atmosphere. Although this reduction is not enough for a complete alloying of compositions such as Co-Cr or Ni-Cr, the hydrogen atmosphere does enable the usage of plastic based binders. These cannot be used in a vacuum furnace due to origination of hydrochloric acid, and subsequent furnace fouling.

5.2 Vacuum furnaces

Vacuum furnaces can be loaded with large lots of materials. They have an internal chamber with a capacity of 400-700 kg of powder. Therefore big lots can be sintered under closely controlled conditions. Actual maximum capacity of this type of chamber furnace is dependent on the specific weight of the material being processed. Temperature is closely and continuously regulated by a cascade PLC control. The whole lot is running through the same sinter cycle and each complete cycle takes 30-36hours typical. The advantage of the vacuum furnaces is the possibility to produce large homogeneous sintered lots. A straight vacuum furnace is limited by the necessity to avoid utilization of some binders, however, modern vacuum furnaces can be run under hydrogen atmosphere during the binder evaporation phase.

5.3 High Pressure Furnace

The construction of high pressure furnaces is comparable to the construction of vacuum furnaces. Only the closing mechanism of the chambers differs to enable a pressure up to 50 bar. This is necessary to sinter alloys or compositions with alloying ingredients that tend to evaporate in the vacuum, e.g. boron. The high pressure prevents this evaporation. These high pressure furnaces represents the "state of the art" in the spray powder manufacturing. All the disadvantages of the other furnaces are solved.

5.4 Plasma densifying

Plasma densifying takes place in an inert chamber. The sintered and crushed powder is injected in a plasma torch and molten. It re-solidifies in a spherical and dense morphology. The flowabillity of the powders is excellent and they are completely alloyed due to the remelting. This method of spheriodization and densification is difficult to control with a level of consistency that allows manufacturing of follow-on lots to have the same characteristics as previous, especially in relation to the formation of the complex carbide phases formed during re-solidification. Plasma densified tungsten carbide solidifies as eutectic cast tungsten carbide and therefore plasma densified powders can produce coatings with the same characteristics of cast and crushed methods. The morphology of the particles will be more compatible with the equipment, but coating brittleness may lead to cracks in the coating.

6. Crushing, Screening and size distributions

After the sintering process, the bricks are crushed and screened into the required distributions. The

crushing process for the purely sintered powders is done with jaw crushers, hammer crushers and air jet crushers. Contamination of the powder with rubbed-off iron dust from the crushers is a serious problem. The iron dust settles down on the powder surfaces and is not alloyed into the metal matrix. Therefore the corrosion properties of coatings produced with sintered and crushed materials might be poor.

In spray dried powders the sintering causes small sinter bridges between the micro pellets. The destroying of these sinter bridges can be done with less energy. The resultant powder particle size is a result of the spray drying process and not of the crushing process. Therefore the use of heavy crushing equipment is not necessary and there is no iron contamination.

Experience has shown that each HVOF system and each customer require a slightly different screen size distribution. It is very important for the powder manufacturer and the end-use to work together to formulate and commit to the exact specifications for the material that will be supplied. The end user should have an understanding and carefully consider the powder manufacturing process. For example, slight changes in the specified size distribution can result in either higher or lower deposit efficiencies. These efficiencies have the potential to be of much greater value to the coating applicator in terms of total coating application cost that does the specifics of the application device type/fuel used. End users and coating applicators should perform a true cost-benefit analysis in respect to the raw materials they are using. This analysis may prove that slightly higher powder cost can often be more than offset by greater deposit efficiency or possibly lowered finishing costs. Also worth mentioning is the coating consumable parts usage rates (barrel/nozzle wear), or machine down-times due to nozzle loading, or rework and scrap production from a process that has interruption(s) in mid-application cycle. All are points worth serious and further detailed consideration.

7. Conclusion

Having in mind the multitude of powders on the market as well as the multitude of HVOF systems it is clear that there is no powder which will meet all requirements. Powders should be carefully understood and completely justified for the application prior to longterm commitments being made. Many failures in applications are traceable to deficiencies in the powder type selected for the application. These mistakes could be avoided by considering all aspects. Only a few problems and interactions of parameters have been shown in this publication. Each difficult application must be discussed between the end user and the powder manufacturer to find the right solution and to consider all aspects. This publication should give the end user an aid to ask the right questions to his supplier. Working together and completely understanding all aspects of the process will allow a greater potential for mutual success

Optimization of Precision Grinding Process

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Gear-teeth grinding of spiral bevel, a costly and inexact science, is perhaps one of the most difficult of all grinding processes. Process development is usually a trade-off between achieving maximum material removal rate without damaging the part. The material removal rate is selected at its lowest possible to avoid any grinding burns. Much longer cycle time and higher percentage of scrap are characteristics of this process. Because the finish grinding is usually the last manufacturing step, any scrap will be relatively costly and takes a heavy toll on the overall manufacturing cost and delivery time. The outcome of grinding process depends upon factors such as materials of the grinding wheel, speed, feed, and in-feed. In this US Army Manufacturing Technology project sponsored by the Aviation and Missiles Command (AMCOM) through the INFAC program at IIT Research Institute, the goal was to improve the outcome of the grinding process, from a quality and cost point of view. The approach involved the utilization of an experimentally proven and well-documented body of knowledge relating to the various parameters involved. A design of experiment (DOE) was established that involved the pertinent variables, the practical value of these variables, how the variables interact, and how they effect the outcome of the grinding process. Based on the DOE, experiments were conducted to better understand the cross functional reactions between the variables. Experimental results showing as much as 50 percent reduction in grinding cycle time can be achieved. This paper will discuss the DOE, grinding, testing, and evaluation of results.

Paper not available

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Materials Of Concern For Gas Turbine Propulsion Systems

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Pratt & Whitney is being driven by market demands, federal regulations, and corporate policies to eliminate the use of hazardous materials in the design, manufacture, and refurbishment of gas turbine engine components. A list of hazardous materials has been identified, based on customer-driven requirements, as well as current and expected U.S. and foreign regulations. A data base has been created that links targeted materials to specifications called out in P&W engine designs. Target materials have been ranked according to relative toxicities that have been prioritized and published by the University of Tennessee and Purdue University. A Hazardous Materials Index has been developed as an important metric to track progress in the development of green components and products.

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Introduction

This paper describes a disciplined approach to identifying and quantifying risks associated with the use of hazardous materials in the design. manufacture and maintenance of gas turbine engines and space propulsion systems. Customerdriven concerns, as well as federal, state, local and foreign regulations form the basis and rationale for the establishment of a Pratt & Whitney materials of concern list. A data base has been established that contains hazardous material information for all of the material and process specifications called out on component drawings. The data base is populated with quantitative data measuring the relative toxicity or hazardous nature of these materials. A hazardous materials index is then defined which is the summation of the individual toxic or hazardous attributes for any engine part, assembly or module, or for the entire propulsion system. The data base and index values drive both component design and material & process development via standard work tools. Aggressive goals for hazardous material reduction are then tied directly to the index and are tracked on a continuing basis.

Background and Approach

Pratt & Whitney has invested significant resources over the past fifteen to twenty years in the development of new material and chemical process technologies. These materials and processes address customer and regulatory requirements by providing non-hazardous alternates for the design. manufacture and maintenance of engines. We have successfully reduced toxic air emissions from our facilities by 99% and hazardous waste by 83% from 1988 to 1999. Ozone Depleting Substances and NESHAP non-compliant handwipe solvents have been completely eliminated in our U.S. operations. Our Standard Practices Manual lists approved alternates for non-compliant materials and for many other hazardous substances.

More recently, Pratt & Whitney has initiated an aggressive Green Engine Program, Figure 1, a rigorous approach to minimizing environmental and health impacts associated with the design, manufacture, use, maintenance and ultimate disposal of our products. We have committed substantial additional resources to the creation of a highly disciplined approach to identifying. measuring and controlling key hazardous materials for propulsion systems. The objectives of this new approach include, first, the identification of a well defined list of targeted materials based on specific regulatory and customer-driven concerns; second, the creation of a data base that documents quantitatively the level of concern of each material and links these hazard values to the material specifications called out for our engine components; third, the definition of a hazardous materials index that clearly measures the environmental and human health impacts of our designs and readily permits tracking of product values on an ongoing basis; fourth, the development of standard work tools that guide the designer in the selection of non-hazardous materials; and, finally, the use of this information to drive the development of new technology to meet aggressive hazardous material reduction goals. An additional future objective is to refine a life cycle cost model that defines the economic value of new technologies.



Figure 1. Scope of Green Engine Program

Materials of Concern

A list of materials that are of specific concern in the gas turbine and space propulsion business has been developed, based on both regulatory and customer input over many years. The U.S. Environmental Protection Agency, the European Union and other local, national and international regulatory agencies have targeted many hazardous materials for control or elimination. For many years, our military customers have required the identification and control of hazardous materials in products manufactured for their use. More recently, commercial customers are restricting or banning the use of certain materials in engines and airframes. The Pratt & Whitney materials of concern list includes the use of all chemicals identified by these bodies that are relevant to our products.

Table I is a list of these materials, divided into three categories, indicating levels of restrictions for use in new designs. The first column contains a list of materials that are prohibited from use, as valid alternates have been approved. The second column lists high-risk materials that are restricted for use, requiring management approval according to a standard work protocol that will be described later. As alternate materials are developed and validated, restricted materials become prohibited for use in new designs. Finally, the third column lists materials that have some negative environmental or health impact and which may be replaced in the future.

Prior to 1994, workers at the University of Tennessee developed an algorithm to quantify and rank the relative hazards of more than one thousand hazardous chemicals. Environmental and health impacts were based primarily on aquatic toxicity factors. From July, 1994 through August 1997, workers at Purdue University modified this approach to include impacts of these chemicals on air quality, potential for soil and groundwater contamination, and stratospheric ozone depletion. They also considered impacts on human health, considering factors such as toxicity, both chronic and acute, and carcinogenicity. The hazard values calculated using the Purdue University rankings were used at Pratt & Whitney to populate a data base linked to gas turbine material specifications as described below.

Materials Of Concern Data Base

The "Bills of Material" (BOM) for Pratt & Whitney engines are controlled by over 2000 industry and internal specifications. A data base was created by surveying (visually inspecting) these documents and recording the "callouts" of prohibited and restricted materials of concern from the list in Table I. The data base was then populated with relative hazard values from the Purdue University study. Since some documents specify the use of multiple hazardous materials, the total hazard value for each specification was determined by summing the individual values for all materials of concern used. In this way, we were able to quantify the environmental and human health risks associated with every specification used in our product designs. This powerful data base could then be used to query bills of material for component, assembly, module and engine designs as described below.

Hazardous Materials Index

The data base described above linked the relative hazard values for materials of concern to the specifications called out on component and assembly drawings. The purpose was to create a tool for quantifying the relative environmental and human health impacts that resulted from our product designs. A metric rigorously determined in this way would provide a highly credible driver for technology development.

A hazardous materials index was defined based on an algorithm used at Pratt & Whitney Canada:

$$I_h = \sum_{n=1}^{IN} T_n * P_n / D$$

where: I_h = Hazardous Material Index N = number of specifications in design T_n = hazard value of nth specification P_n = number of part numbers that call out specification n D = total number of part numbers in the design

For any component, assembly, module or engine, the Hazardous Materials Index, I_h , is defined as the summation over all the specifications in the design of all the specification hazard values, multiplied by the total number of specified parts used and normalized to the total number of parts in the design. By normalizing the total hazard value, products of different size and complexity can be compared to identify the biggest impacts and opportunities for improvement. The hazardous materials index can be used to set quantifiable goals and track progress in attaining them. Table I Materials of Concern

Prohibited

Restricted

Arsenic & compounds Asbestos Benzene Beryllium Cadmium & compounds Chlorinated solvents Ethyl alcohol Ethylene glycol ether compounds Formaldehyde Mercury & compounds Methanol (methyl alcohol) Methylene chloride Class I ozone depleting substances Radioactive materials, Including thoriated (TD) nickel Toluene diisocyanate

Chromium, hexavalent Class II ODS Cyanides Dimethylformamide HCFC-14 lb & HCFC-22 Hydrazine Hydrofluoric acid Hydrogen fluoride gas Lead & compounds Manmade fibers, e.g., cristobalite, fiberfrax MDA (4', 4'- Methylenedianiline) Methyl alcohol (methanol) Methyl ethyl ketone (MEK, 2butanone) Methyl iso-butyl ketone (MIBK, 4-methyl-2- pentanone) Phenol Styrene Toluene Xylene

To Be Reduced

Acetone Ammonia Butyl alcohol Ethyl benzene n-Hexane Hydrochloric acid Isocyanates n-methyl-2- pyrrolidone Isopropyl alcohol Nickel plate Nitric acid Petroleum distillates (e.g., Naptha, Mineral Spirits, Stoddard Solvent, Varsol, evaporative lubricants) Phosphoric acid Sec-butyl alcohol Sulfuric acid 1, 2, 4-Trimethylbenzene







Figure 3. Restricted Materials Of Concern – Legacy Engines

A hazardous materials index can be easily calculated for prohibited and restricted materials of concern, separately. Figure 2 illustrates how the use of prohibited materials of concern has decreased substantially in newer engines, compared to legacy designs. Figure 3 illustrates that although some progress has been made in the elimination of restricted materials, the opportunity to improve is substantial. Considering the trends in these two figures, it is obvious that the index for prohibited materials is driving technology development needs for mature engines, while the index for restricted materials is driving technology for new designs. The latter technology then flows down through our legacy products via the specification change process.

Figures 4 and 5 illustrate how technology links directly to the hazardous materials index for a current generation engine. The percent contribution to the total index by any specific material of concern can be easily extracted from the data base for any particular engine. For instance, eliminating leaded dry film lubricants and silver plated fasteners from the PW6000, currently being developed, will result in a reduction of the restricted materials index by 26.6 %. Eliminating chromates in the form of chromic acid anodize, conversion coatings, primers and chrome plate will reduce the index by another 33.8%. The estimated life cycle cost savings is also shown in these figures. Our life cycle cost model is currently being refined and will be the subject of a future paper. While technology is being developed to replace other materials shown in the figures, clearly our greatest focus is on the big hitters.

Design Standard Work

The materials of concern data base is linked to drawing specifications and has enabled the creation of a standard work tool for designers. A standard work protocol facilitates the selection of "green" materials and processes for new designs. Figure 6 shows schematically the materials design and approval process. The tool contains background information, technical contacts and protocols. It references a list of material and process specifications that contain materials of concern. The designer can also link to the data base containing materials of concern and hazard rating detail. Finally, it links to a menu for selection of alternate materials and processes, cross-referenced by specification.

Green Materials And Processes For The PW6000

Figure 7 summarizes our technology development program to replace materials of concern in the PW6000 engine. It is anticipated that lead, cadmium and chromate alternates, in addition to elimination of xylene and toluene in manufacturing processes, will result in a dramatic reduction of the hazardous materials index compared to recent generations of engines.

Summary and Conclusions

The vision of green gas turbine and space propulsion systems is rapidly becoming a reality at Pratt & Whitney. Hazardous materials in our products and processes throughout the life cycle are aspects of the green engine that are receiving high priority. The disciplined approach described in this paper has helped to create a technology development roadmap based on credible and accurate data. Materials of concern have been identified based on customer- and regulation-driven requirements. Relative environmental and human health impacts have been documented using a credible academic study. A powerful data base has been constructed that has been linked to design specifications and is used to query product bills of material for hazardous material content. Accurate documentation and mapping of hazardous materials applications throughout the product design can be accomplished. A hazardous materials index has been defined to accurately characterize environmental and human health impacts and is used to compare products of different size and complexity. It is also used to accurately gauge progress toward attainment of quantifiable goals. Most importantly, the index identifies areas of greatest toxicity and associated life cycle costs and drives development of technology. A standard work tool has been created to guide designers in the selection of materials and processes. Finally, the development of a new generation of "green" engines, starting with the PW6000, can be credibly documented publicized. and



Figure 4. Percentage Contributions From Lead And Cyanide To The Hazardous Materials Index For A Legacy Engine



Figure 5. Percentage Contributions From Chromates To The Hazardous Materials Index For A Legacy Engine



Figure 6. Schematic – Standard Work Protocol



Figure 7. Green Materials and Processes For The PW6000

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Improvements in Blasting Process Media

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The development of the plastic media blasting process has been a 20-year progression of improving medias, equipment and process parameters. Today, engineered abrasives (with physical characteristics designed into the particles) are tailored to diverse aerospace surface and coating requirements. The latest media development is a nanocomposite that combines polymer, nanostructure and composite technologies to remove coatings faster without damage to a wider range of substrates.

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IMPROVEMENTS IN BLASTING PROCESS MEDIAS

By: Raymond F. Williams

Abrasive blasting with loose abrasives has evolved over centuries. Abrasives used initially were sands, and other naturally occurring minerals. With the industrial age came slags, which were by-products of smelting, and agricultural by-products such as nut hulls and pits. Throughout this period the physical characteristics inherent to the material were adapted to. Today, desired physical characteristics are engineered into materials in order to make them capable with the substrates, coatings, and desired results.

Abrasives historically were measured on a MOHS scale originally designed to measure the hardness of minerals. The MOHS scale goes from 1-10, with 10 being diamond hard. Historically, it ranged from soft sands, which began around a 5 hardness, and went up to aluminum oxide, silicon carbide, and diamond, in hardness. Agricultural abrasives started around 2.5 and became softer going from walnut pits through corncobs and rice hulls. But, there was always a gap in the middle, in the 3-4 hardness range. Plastic medias developed in the early 1980's fit into this hardness range and made possible applications not previously feasible with existing abrasives. With plastic abrasive came the concept of a material that was harder than the coatings it was removing, but softer than the substrate beneath.

The first plastic abrasive developed was unfilled polyester. Throughout the 80's and early 90's, plastic abrasives utilized in abrasive blasting were still identified and used accepting their existing physical characteristics and properties. In order to adapt these abrasives to different applications, particle size and other process parameters were adjusted. Polyester being fairly soft was considered a very delicate abrasive and was widely used in electronics for cleaning printed circuit boards, and in some aerospace applications for coatings removal from composites and thin-skinned materials. However, on modern coatings, polyester

was not considered to be fast enough for large production depaint operations, which lead to the development of the second material. Type II, which is urea formaldehyde. While polyester raw material had come from the button industry, urea formaldehyde was traditionally used in the electronics industry for light switches and wall plate covers. These materials fell within the family of thermosets, which are plastics which cannot be reheated and reformed. Type II, urea, became an industry workhorse, being highly productive and durable. It was reinforced with alpha cellulose fiber and could remove coatings at a high rate of speed. Type II was extensively used on aircraft becoming the media of choice for depainting the entire fleet of F-4 Phantom fighters and CH-47 Chinook helicopters. During that period of time, Republic Airline also stripped a number of commercial aircraft prior to their acquisition by Northwest. During these early days, the processes were very operator sensitive with narrow margins of error and required a high degree of control of process parameters. Today, Type II medias are primarily used for engine overhaul, component cleaning, landing gear, wheel and brake, AGE equipment and other durable components of the Outside of aerospace, it is used in manufacturing aerospace industry. processes, cleaning castings, molds, and other hardened aluminum or steel components. In some instances, it is used for profiling softer substrates such as graphite epoxy. The third abrasive to come along was melamine formaldehyde, which primarily comes from the non-breakable dinnerware industry. Type III media was harder than the Type II and had a hardness of 4.0 on the MOHS scale. This material has principally been used for removing tenacious powder coatings and cleaning harder coatings or contaminants from durable surfaces. Melamine in fine sizes is also extensively used in the integrated circuit industry for deflashing.

Type IV, phenol formaldehyde, did not prove popular with users and the next material developed was a high molecular weight cast acrylic. Type V acrylic had a hardness of 3.0 but had a reduced density of 1.2 combined with durable cutting edges and reusability. For the past 10 years, Type V acrylic has been the

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preferred media for dry stripping of military aircraft exteriors. Combined Type II and Type V history includes over 15,000 aircraft that have been successfully depainted using plastic abrasives. This includes the entire fleet of C-5s and most C-130s, plus F-16, F-18, F-14, F-17, fighters, trainers (T-38), attack aircraft (A-10), and rotary wing aircraft, including Sea Stallions, Chinooks, and Hueys.

The plastic media dry stripping process takes place within a confined area to keep the material free of contamination and to recover it for reuse. Equipment designed for this purpose recovers and cleans material prior to its reuse. This can be from as simple as cyclonic separation of dust to a complex system with dense particle separators, magnetic cleaners and sieve systems. The size of the systems ranges from cabinets, to full hangars for wide-bodied aircraft. The largest dry media dedicated facility is operated at Boeing Aerospace Support Center in San Antonio, and will house a C-5 or 747 size aircraft.

Critical to the use of plastic abrasives is process parameters control. The process parameters include particle size and shape, particle hardness and density, air pressure at the nozzle, media flow rate, nozzle size, stand-off distance which is distance from the nozzle to the surface), and the angle of attack. Each of these parameters is important and changing any one will change the resultant affect of the blasting and potentially the affect on the substrate.

In the early 1990s came the first attempt at engineering an abrasive to the requirements of a substrate and application. That effort resulted in a starch graft co-polymer identified as Type VII, which combined crystalline starch technology with acrylic by grafting them into a single molecule. This resulted in an abrasive which had unique capabilities and delicacy in substrate protection. However, commercial and military customers demanded higher productivity rates, lower fatigue rates, and greater cost effectiveness as compared to chemical strippers.

The second engineered plastic abrasive to be developed is an nano-composite material. Nano-sized particle engineering promises to be one of the greatest enhancers of physical, mechanical materials enhancement capability in the next 20 years. Opportunities are being developed in medical, metallurgical, and polymer sciences. One of these nano-sized structures developed in the thermosetting polymer arena is montmorillonite clays. These are produces in impermeable transparent sheets, having individual platelets, one nano-meter thin, but with the surface dimension extending to 1,000 nanometers. In the case of a nano-composite blast media, these particles are disbursed into a blend of amino-thermosetting polymers. When laid out, the montmorillonite materials are one-billionth of a meter thick and 750 sq. meters per gram. Small amounts of these nano-clays can have large affect on the rheological, structural, thermal, and barrier characteristics of base polymer.

The term nano-composite is relatively new and requires some explanation. For our purposes, a nano-composite is a polymer system containing an inorganic particle with one dimension of one-billionth of a meter in range. This is then compatiblized in an organic polymer such that the clay is chemically modified or intercalated in the polymer such that the spaces or galleries between the clay surfaces are filled. Because the surface area of nanometer sized particles is so large, small amounts of the additives can have an intimate relationship with the polymer and cause significant changes in the polymer behavior.

Toyota R&D labs initially conceived polymer clay nano-composites about ten years ago. By observing that most reinforcing materials in polymers, such as glass fibers, were not homogenously dispersed at the microscopic level, they theorized that a finely sized layer platelet would improve properties.

In the case of nano-composite abrasive, the nano-composite media is more efficient in coating removal by maintaining more durable surface integrity and cutting edges. This equates to a faster paint removal rate, less dwell time, and

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consequently, less fatigue to the substrate. By combining known particle characteristics in terms of size and shape with controlled process parameters, this one type of media is able to address a broad range of surfaces from clad to thin-skinned, honeycomb, and composite. It is the nature of aircraft today that they have beneath the coatings a wide range of substrates such that one media process, which is able address all of them, is desired.

Boeing has approved nano-composite Type VIII media for use on the KC-135 fuel tanker, B-52 bomber, and C-17 cargo aircraft. The current approval is for metals and additional aircraft systems approvals for metals and composites is in testing. Boeing materials characterizations studies in the structural testing labs found an improvement in fatigue life over baseline coupons. Of all media studied to date by Boeing, this is the first to actually improve fatigue life. The Air Force has included nano-composite type media as Type VIII under mil spec for plastic media and this material is in production use at the B.A.S.C. facility in San Antonio where 35 aircraft have been depainted with it over the past year.

Another development in the abrasive world is sponge media. Sponge medias come in abrasive and non-abrasive forms. Non-abrasive forms can be loaded with chemical or water to enhance cleaning capabilities. Sponge media can also be loaded with a wide range of standard abrasives including aluminum oxide and steel grit. The cleaning mechanism of sponge media is different than loose abrasives. While loose abrasives, whether plastic or mineral, chip the paint or contaminant from the surface, sponge medias flatten on impact with the surface and scoot across the surface dragging their abrasive. Because of this difference in mechanism, sponge lends itself to finely controlled processes for very lightly abrading or selective layer removal of coatings. The other benefits of sponge medias are they have a very low dusting level, and bounce back of the particles after impact. Due to these characteristics, the material is currently in testing for fuel tank interior cleaning, and other confined space applications. The ability of sponge media to selectively strip coatings or lightly abrade only, has created

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opportunities to replace hand sanding operations or scuff sanding prior to over coating.

Abrasives have continued to evolve in their ability to more accurately differentiate between the hardnesses of coatings and substrates. The range of physical characteristics of the medias combined with size and process parameters now create a broad spectrum of capabilities in surface preparation, cleaning, and depainting. From the days of sandblasting, which was dirty and aggressive, to dustless selective stripping of single layers of coatings from delicate surfaces, the dry stripping process have come a long way. Materials will continue to be developed to specific capabilities and applications to meet the evolving needs of industry.

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Abstract:

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The quality of Type III anodic coatings formed on casting AlSi7Mg (AA 356.0), sand cast under twenty-one different conditions, varies significantly from casting to casting. The anodic coatings are formed by pulse anodized using the Yokoyama pulse technique and the formation of alumna is mainly made in sulfuric acid as in conventional hard anodizing.

Depending on specifications (technical performance or coast reductive circumstances), significant improvements can be achieved by combining knowledge within the casting industry with knowledge from the hard anodizing industry.

The results of this research project clearly illustrates that the differences in the outcome of hard anodizing castings from job shop to job shop could also be a result of variation in the quality of castings from one casting operation to another. Hence a casting is not necessarily a casting. The technical performance and quality of the oxide film may vary significantly even though the alloying constituents are identical.

Introduction

It is well known that different aluminum alloys have to be anodized differently. Also alumna properties change from one anodizing job shop operation to another because the process conditions of the surface treatment are not identical. At the same time, one specific cast alloy anodized identically might have different properties because the quality of the alloy varies. The conditions of the aluminum surface are highly dependent on the casting conditions such as modification of the melt, addition of grain refiners, hydrogen content, feeding temperature, the mold type, etc.

The purpose of this study is to combine the knowledge within the casting industry and surface treatment of aluminum, thereby produce sand cast aluminum with an optimum surface for production of high quality oxide coatings. This paper summarizes some results obtained when seven different casting conditions along with modification of the mold are pulse anodized in sulfuric acid and in a proprietary anodizing electrolyte called U-Acid ("U"="Unknown"). The objective is not too explain why the technical qualities of the oxide coating varies by merely to identify the range of variation of

the hard coats and the best casting conditions for anodizing.

Pulse Anodizing

The pulse anodizing technique in the Yokoyama process (Y-process) uses square formed pulses of 5 - 100 seconds duration (1). The main objective is to disperse the heat generated and to control the morphology of the oxide produced during galvanostatic or potentiostatic anodizing. The alumna formed consists of a multilayered structure, where thin layers of smallsized unit cells separate thick layers of largesized unit cells. The heat generated during a pulse period at high current is dispersed in the following period where the current is low. This makes it possible to form thick and dense oxide layers without the occurrence of burning.

The advantage of using pulse anodizing versus conventional direct current (D.C.) anodizing is the strongly increased number of independent parameters controlling the anodizing process. The final result of the surface treatment depends on the applied pulse pattern, the electrolyte, and the aluminum substrate. The optimum conditions have to be determined through experiments, although some general guidelines do exist.

Experiments have shown that it is possible with the Y-process to form a thick and compact alumna that is superior to oxide coatings formed during conventional D.C. anodizing at low temperatures (2,3). Furthermore, is has also been shown that coatings produced in U-acid are superior to aluminum pulse anodized in sulfuric acid (4).

Casting of aluminum

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A liquid metal is a highly reactive metal. It will react with both the gases above it and the solid material, which contains it. The driving force for these parameters are the striving of the melt to come into equilibrium with its surroundings. Its success in achieving equilibrium is limited by the rate at which reactions take place and the time available. When the liquid metal enters the mold, it reacts violently resulting in changes to the shape of the mold. Therefore, much work has been carried out in effort to increase its rigidity. Greensand has been the most used casting process during history and addition of clay (Bentonite) is one method of enabling a denser and harder mold to be made. The action of the clay is complex: not only is it important as the main component of the binder, but it also shrinks appreciably on drying, helping to counter the expansion of the sand during heating. Mold surface failures because of thermal expansion can be reduced or eliminated if the sand is added Chromite or zircon.

The most important reaction at the metal surface is the reaction of the metal with water vapor, which results in a surface oxide and hydrogen evolution. Hydrogen from a surface reaction can diffuse sufficiently far in time available during the solidification of a casting and thereby contribute to the formation and growth of subsurface porosity.

When the conversion from liquid to solid occurs, it is first by a process of nucleation and then by growth. Nucleation is the process of the aggregation of clusters of atoms, which represents the first appearance of the new phase. Growth is self-evidently, getting bigger. The nucleation process can be influenced by a number of metals. Grain refinements are achieved by addition **of** Sodium (Na) and Strontium (Sr).

Experimental

The alloy used in this survey is AlSi7Mg0.3 made by Elkem Aluminium from a series called Sibloy. A chemical analysis of the alloy is shown in Table 1. The casting temperature is 700°C (1292°F) and all castings are bars with a diameter of 36 mm. The conditions investigated are as follows:

1. Chill casting with a very high cooling rate (47 seconds calculated on the dendrite spacing). The productivity of this method is low (8 to 10 casting per hour) and the expenses high. The needs for an insulating pasta and a controlled cooling rate are two more drawbacks.

2. Quarts sand added Chromite, where the mold is bound chemically by Sodium Silicate. The addition of Chromite reduces the thermal expansion of the mold, reducing the risk of surface failure of the casting. The cooling rate is fairly low and the expenses fairly high because of Chromite.

3. Magnetite is a mixture of silica sand and iron ore. The cooling rate is fairly low: 104 seconds. The operating costs are low and the productivity is very high (360 castings per hour).

4. Quarts sand bound chemically by sodium silicate (Quarts) has a very low cooling rate: 175 seconds. The productivity is high (360 castings per hour) and the production costs very low. The risk of surface failure is present because of thermal expansion of the mold.

5.Quarts sand bound with clay (Quarts/Bentonite) has a fairly high cooling rate because of the water content: 85 seconds. The productivity is high (as quarts) and the production costs are low.

6. Quarts sand and iron ore bound with clay (Magnetite/Bentonite) has a cooling rate which is comparable to chill casting: 55 seconds. The productivity is high (as quarts) and the production costs are low.

7. Quarts sand added Zirconium has a fairly high cooling rate: 80 seconds.
LIEITIEITIS	AI	Si	Fe	Mg	В	
W/w %	92.48	7.16	0.09	0.25	0,02	

Table 1. AlSi7Mg: Composition analysis of the castings used in the experiments.

Also investigated are unmodified melts and melts added grain refiners Sodium (Na) or Strontium (\$r), which increase the total number of casting conditions investigated to twenty-one (21).

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All the sides of the cast bars are mechanically machined $(Ra\approx1\mu m)$, leaving only the top and bottom areas in "as cast" conditions. The surface roughness (Ra) is measured on the mechanically machined surface before and after anodizing (n=5).

Each bar is numbered randomly in order to minimize subjectivity. Pulse anodizing is made in 15 w/w % sulfuric acid at 14°C. The process time is 50 minutes. The pulse conditions are 4 A/dm² for 60 seconds followed by 1 A/dm² for 20 seconds. The pretreatment consists of degreasing and bright dip in 50 v/v % nitric acid. Pulse anodizing in the proprietary U-acid electrolyte is produced with a pulse pattern under process conditions, which maximizes microhardness of the anodic coating.

The thickness of the oxide coating is



Figure 1. The cooling rate of the castings investigated measured as dendrites spacing.

measured microscopically on a cross section (n=10). The homogeneity of the coating thickness is represented by the Standard Deviation (St. Dev.) of the measurements. The microhardness is measured as Vickers Hardness with a load of 25 g (n=8) on a cross section.

Results

The solidification profile measured as solidification time, in the seven castings investigated is presented in Figure 1. The solidification time is calculated using the spacing of the dendrites, which is correlated with the conditions during solidification. Investigated are cooling rate from 50 seconds to 175 seconds.

The anodic formation rate is highly related to the anodizing potentials of the surface. It is well known that cast surfaces anodizes at a slower rate that machined surfaces. It is nicely illustrated in Figure 2, where the coating thickness is significantly higher on the machined surfaces. And in addition within each surface category ("machined" versus "as cast"), a large variation is also noticed.

On the machined surface the maximum thickness after 50 minutes of pulse anodizing at elevated temperature is approximately 90 μ m. This corresponds to a formation rate of 1.8 μ m/minute, which is close to a doubling of the formation rate in conventional Type III anodizing. The lowest thickness measured is close to 55 μ m, which is close to a formation rate experienced in conventional hard coat anodizing. However the difference is a result of the conditions of the castings, not the anodizing conditions.

An uniform coating thickness over a part, which contains "machined" and "As Cast" surfaces, is important for the corrosion



Figure 2. The anodic coating thickness on the castings investigated. The thickness is measured cross sectional and represents the average of 10 random readings.



Figure 3. The difference (%) in coating thickness between "machined" and "as cast" surfaces versus the casting conditions investigated.

protection. Depending on the conditions during solidification of the molds, some conditions reduce the difference in thickness between machined and as cast surfaces significantly (sample#12 and #21 in Figure 3). However some casting conditions results in a difference close to 50%.

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Another important factor influencing not only corrosion performance, but also wear performance is the variation in coating thickness within a casting. Figure 4 illustrates relation between the the thickness homogeneity calculated as 95% C.L. on the Standard Deviation of the cross sectional measured thickness (n=10 per sample) for casting produced without grain refiners. The trend line of the data does not indicate any correlation between solidification rate and thickness uniformity. The situation is different if the molds are added the grain refiner Strontium (Sr). The higher the cooling rate is, the smaller is the thickness variation (Figure 5).

During conventional direct current Type III anodizing, surface roughness prior to processing is known to increase significantly after oxide formation. The increase can be as high as 400-500% for castings.

Figure 6 illustrated the increase in surface roughness (R_a) for the casting conditions investigated with addition of the grain refiner Strontium $reflect{Fr}$). Obviously the data show that a fast cooling is appropriate if the increase in surface roughness must be low. However, the data also shows that when the cooling times is 80 seconds and higher, the solidification process do not influence the change in surface roughness. Worst-case scenario is cooling rates at around 75 seconds.

Microhardness is another property important for characterizing the technical quality of an aluminum oxide coating. It is generally accepted that during conventional anodizing microhardness decreases as thickness increases. In pulse anodizing microhardness is independent on processing time, hence thickness (4).

The data shows the relation between microhardness and thickness known from



Figure 4. The uniformity of the anodic coating calculated as 95% C.L. of the standard deviation from the cross sectional thickness measurements for casting without addition of grain refiners versus cooling rate



Figure 5. The uniformity of the anodic coating calculated as 95% C.L. of the standard deviation from the cross sectional thickness measurements for casting added Strontium (Sr) as grain refiner versus cooling rate



Figure 6. Increase in surface roughness (Ra) versus cooling rates for castings added Sodium (Na) as a grain refiner.

conventional anodizing is also present when anodized using the pulse technology if the casting is added Strontium (\$r) as a grain refiner (Figure 7). The correlation between microhardness and coating thickness is not present if the castings are made without grain refiners (Figure 8). Obviously, the correlation between casting quality and the microhardness of the anodic coating formed during anodizing is complex of nature.

Microhardness could be related to the conditions during solidification. At least it is an option. However the data from this research project do not support any correlating between the casting conditions and the microhardness when anodizing is made in sulfuric acid (Figure 9).

Obviously the microhardness seems to be more dependent on the anodizing conditions and not so much on the cooling conditions during solidification of the castings. However, the relation between coating thickness and microhardness is to some degree related to the grain size, which illustrated by the results in Figure 7 and 8.

If the microhardness is mainly related to the anodizing conditions a change in anodizing chemistry should result in changes microhardness.

Pulse anodizing in U-acid do show that the conditions during casting (here measured as the cooling time) is independent on the microhardness (Figure 10). It also shows that the chemistry of the



Figure 7. Microhardness versus coating thickness for castings added Strontium (Sr) as a grain refiner



Figure 8. Microhardness versus coating thickness for castings without a grain refiner.



Figure 9. Microhardness and cooling time for the casting investigated.



Figure 10. Microhardness of anodic coatings from anodizing in Sulfuric Acid and U-Acid for castings without addition of grain refiners

electrolyte is an important factor controlling the technical quality of the anodic coatings.

The microhardness values achievable in U-acid are approximately 200 $HV_{0.025}$ higher than when anodizing in Sulfuric Acid electrolytes.

Conclusion.

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In relation to job shop operations, the experiments have shown that if an oxide coating fails a quality test and all anodizing parameters are within tolerance, it is likely that the failure is related to the quality of the casting process. These results could be from either a change in the casting conditions or because the customer has changed to another supplier of castings.

The experiments also show that if high quality of the oxide coatings is a priority, it is important that the surface finisher become involved early in the development of a product. The advantages are increased overall quality by being involved in the recommendations of the casting conditions or help identifying the optimum conditions for the casting process ensuring maximum anodic coating performance.

Acknowledgments.

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In Tank Removal of Hard Chromium Plating Contaminants

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BASX Systems, LLC has successfully removed contaminants from a hard chromium plating system utilizing a ceramic microfilter. This process uses the microfilter to remove trivalent chromium and iron from the plating solution without reducing the hexavalent chromium solution. The solution is then adjusted back to meet the specifications of the tank and returned to the plating tank. This is performed on a skid-mounted system next to the plating tank. The other solution generated by the hard chromium plating process is a wastewater from the ion exchange system. We were also able to successfully reduce the volume of the wastewater treatment solution from this process by using the microfilter. Volume was reduced from 1,000 gallons of wastewater disposed of off site per week to a solid form of less than 50 pounds per week. This paper will discuss these two processes, what was learned from this research project and what potential this project has for a full-scale system.

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Introduction

Hard chromium plating is an important process in the airline and aerospace industries. This plating process incorporates special features:

- □ Thicker coatings
- □ High hardness
- □ High abrasion resistance
- **Corrorsion resistance**
- □ Heat resistance
- □ Low coefficient of friction

In recent years, the metal finishing industry has found new ways to reduce the effect of hard chromium plating on the environment. New measures have been taken to reduce the amount of mists from the hydrogen generation during the plating process through fume suppressants.¹ One of the concerns for the metal finishing industry is the proposed Metal Products and Machinery (MP&M) regulations, which will require metal finishers to meet new stringent standards regarding chromium and the contaminants in the hard chromium bath.²

Due to contaminants in the hard chromium process, the bath needs to be wasted even though many of the components are still viable. The removal of these contaminants will be the focus of this paper.

Constituents of the Hard Chromium Bath

The deposition of chromium is normally performed with one of two solutions. The two solutions are either trivalent chromium or hexavalent chromium. Hard chromium plating is performed with hexavalent chromium or hexavalent chromium oxide (CrO_3). Chromium plating is operated with insoluble anodes, so that all of the metal deposited is taken from the solution and must be continuously replaced.

No metal can be deposited from solutions of pure chromic acid. Small amounts of foreign anions or catalysts need to be present. These catalysts are normally sulfate. fluoride. silico fluoride or fluoborate. If there is not enough catalyst, then the hard chromium plating process will not operate properly. If there is too much catalyst, then the current density will increase to unacceptable levels. Therefore, it is important to have the correct ratios of catalyst in the plating bath. These conditions are provided in Table 1.4

Table 1		
Condition	Low Conc. Solution	High Conc. Solution
Chromic	250 g/L	400 g/L
Acid		
Sulfuric	2.5 g/L	4.0 g/L
Acid		
Current	31 to 62	16 to 54
Density	A/dm^2	A/dm^2
Temp.	52 to 63 C	43 to 63 C

Note that the ratio for chromic acid to sulfate or sulfuric acid is 100:1. This is an important ratio to keep in balance within the system. This ratio can vary between 80:1 and 120:1.

Contaminants of Concern

There are various contaminants within a hard chromium bath that will cause the plating process to malfunction. Theses contaminants are:

- **□** Trivalent chromium
- □ Lead
- □ Copper
- **C**admium
- □ Iron
- Nickel
- □ Zinc
- □ Aluminum

Trivalent chromium results from the reduction of the hexavalent chromium in the plating process and will result in an increase in the current density. The lead results from the anodes used in the process. The remaining metals are normally a result of the basis metal or the metals used in the process.

In order for the hard chromium process to function properly, these metals must be kept below various levels. Normally, the trivalent chromium is kept below 1.5% of the solution strength. The remaining metals should be kept below 100 to 10mg/L.

Experimentation

The experiment was designed to remove these metals and contaminants without wasting the hard chromium bath. This process would take a split stream of the hard chromium bath, raise the pH to precipitate the divalent and trivalent metals while leaving the remaining hexavalent chromium. This can be performed by utilizing a hydroxide precipitation step. Hexavalent chromium will not precipitate to any extent as a hydroxide. In order for this process to be successful, the materials of construction are very important. We utilized a ceramic microfilter for the removal of the precipitants. This is provided in Figure 1.



Figure 1 – Ceramic Microfilter

We were able to successfully remove the divalent and trivalent ions from solution. These results are provided in Table 2.

Parameter	Influent mg/L	Effluent mg/L	Goal mg/L	
Aluminum	15.3	< 0.2	<10	
Copper	123	2.3	<10	
Tri-	6,300	1,170	<15,000	
Chrome				
Hex-	55,700	50,000	250,000	
Chrome				
Iron	976	0.5	<100	
Lead	10.3	< 0.2	<10	
Nickel	2.2	0.8	<10	

This experiment was performed at a pH of 5.0. The pH was raised by adding a considerable amount of sodium hydroxide. As shown by the table above, we were able

to successfully remove the contaminants of concern. However, during this process, we also diluted the hexavalent chromium. We also added a considerable amount of sodium to the solution, which will eventually become a problem. In order to reduce the amount of chromium needed, we attempted to utilize hydrogen peroxide (H_2O_2) to precipitate some of the metals and reduce the amount of sodium hydroxide needed. This reduced the metals to below 10 mg/L, but did not work as well as the hydroxide precipitation.

As shown by the results, this solution can be readjusted to meet the 100:1 ratio of chromic acid to sulfuric acid. However, we did not believe this would be economical.

Reduction of Ion Exchange Solution

The second aspect of this research was to reduce the amount of waste that was being generated. As part of the waste solution process, approximately 1,000 gallons per week were being wasted from this facility. We were attempting to reduce the amount of solution or waste from this process as part of a pollution prevention program.

The experimentation was intended to reduce the hexavalent chromium solution to trivalent chromium and then reduce the amount of solution. The process is provided in Figure 2.



Figure 2 – Ceramic Microfiltration Wastewater System

This process was able to meet the required 40 CFR 433 discharge standards for the local municipality. In addition, the 1,000 gallons of solution that was being discharged off site was reduced to approximately 50 pounds of solid material. Both materials would be classified as a hazardous waste, but due to the volume reduction, this was a much lower cost option. The payback on this type of system is approximately two years.

The above process requires the reduction of the hexavalent chromium to trivalent prior to raising the pH to remove the metals as a hydroxide. We are currently researching a different process utilizing electrocoaguation, which has shown very positive results. This would lower the chemical requirements considerably, due to the precipitation occurring in the hexavalent state and the reduction of hydroxide as this precipitation occurs at a low pH.

Conclusions

There is a definite need to research the reduction of environmental impact by h hard chromium plating. To date, processes have been developed to reduce the fumes from this process. What is needed is a reduction of the effects of the waste treatment solution.

This research provided a proposed method of reducing the need to regenerate the solution of the hexavalent chromium bath by removing the contaminants in-situ. While this process was able to remove these constituents, the cost is not practical at this time.

This research also reviewed the treatment of the waste solution from the regeneration of the ion exchange solution. This process was successful in reducing the waste solution of 1,000 gallons per week to a solid form of 50 pounds per week. This resulted in a payback of two years.

We are currently investigating the use of electrocoagulation for this process. This coagulation step appears to hold great promise regarding the removal and reduction of chemicals utilized in this treatment process.

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Improved Threaded Fastener Coatings for Turbine Engines

Dr. Paul Sutor, Surfaces Research, Lenexa, KS

Many fasteners in turbine engine hot sections seize and break upon removal, despite the use of silver anti-seize coatings. Overhauls require extra labor, and collateral turbine damage occurs. Silver also corrodes titanium alloys, embrittles engine superalloys, and migrates above 1200°F. Improved anti-seize coatings have been developed that have better properties than silver, remain stable and adherent at 1500°F, and are completely benign to engine alloys. Fastener failure analyses and coating performance tests will be presented. The U.S. Air Force estimates that \$25 million in annual maintenance costs can be saved by using the improved coatings.

Paper not available

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Technology Use at Tinker AFB

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At the onset of toxic release reporting in 1994, Tinker AFB generated 1.8M pounds of toxic releases to the environment. This was enough to make TAFB the largest emitter of toxics in the Department of Defense (DoD). Today, Tinker has reduced its emissions by more than 84 percent through aggressive pollution prevention actions. This paper addresses technologies used to reduce the Toxic Release Inventory (TRI) emissions for the base while allowing production needs of this aerospace maintenance facility.

For more information contact: Geri Hart OC-ALC/EMV, Building one 7701 Arnold Street Tinker AFB, OK 73145 (405) 734-7071 In the 20th Century, world markets for environmental technologies grew dramatically. Promoting these environmental technologies has been a high priority for Tinker AFB and an exciting opportunity to achieve environmental and occupational safety goals for the base. In addition, having a clean environment and being a good neighbor means a lot to us.

One area where technology insertion has been apparent is with our implementation of Executive Order (EO) 12856. This EO requires that federal facilities comply with all the provisions of the Emergency Planning and Community Right to Know Act (EPCRA) and the Pollution Prevention Act of 1990. In plain language the air force must take an inventory of over 600+ toxic chemicals and report their usage and release levels to the public. Aircraft maintenance and repair, such as that performed at Tinker AFB, involves four major industrial processes: Electroplating, Cleaning, Painting and Depainting. Over twenty-five toxic chemicals were reported to EPA under this program in the 1994 baseline year.

Tinker has taken giant strides by reducing some 84 percent or 1.5 million pounds of toxic emissions in just seven years. Much of the success is a result of our ability to seize leading edge technology many times in the developmental phase and implementing it in our critical processes. The maintenance or production areas at Tinker have been proactive in implementing these technologies, which have saved time, manpower and cost for environmental factors (e.g., disposal, material costs, etc). Furthermore, under the canopy of technology transfer these innovative improvements in production are continuously transferred among DoD, regulatory and scientific communities.

Tinker has led the AF in reducing ODC's and TRI chemicals. Through an active, close working relationship with the Environmental Protection Agency, HQ Air Force Material Command and other Air Logistics Centers the Air force has proven it's dedication to reducing TRI chemicals. Outstanding accomplishments in reducing TRI emissions include implementation of the following technologies:

- Electromechanical Device Cleaning Systems. During aircraft depot maintenance, effective cleaning operations to prepare parts for coatings and to degrease re-furbished parts are crucial. Parts washing cabinets that enable the use of high quality aliphatic hydrocarbon solvents are now in operation. Formerly, parts were cleaned through immersion in vats containing high concentrations of chlorinated solvents such as 111 Trichloroethylene and Chlorofluorocarbons. This more advanced technology has eliminated some 15,000 lbs of air emissions each year.
- Electromagnetic Powder Deposition (EPD): EPD is used to replace Chromium, Cadmium, Nickel and Silver plating. This process uses an electromagnetic field to accelerate particles from 2 to 30 kilometers per second. The kinetic energy is converted to thermal energy on impact; thereby melting the particles in a localized

area of impact. This process replaces the traditional plating process that utilized vats of very hazardous materials such as acid baths, cyanide, etc. The Electromagnetic Powder Deposition process reduced annual wastewater discharges by over 19 million gallons and reduced hazardous wastes by some 228 tons per year.



Electropowder Deposition

• **Pressure Spray Washers:** Fourteen vapor degreasers were replaced with pressure spray washers. The vapor degreasers had been used to clean aircraft parts. This alone reduced our hazardous waste by some 100,000 pounds/yr. Likewise, this action cut down our air emissions by about 130,000 pounds/yr.



High Pressure Aqueous spray washer

• Acid Etch Rejuvenation: Tinker, the Department of Energy and private industry joined forces to develop and apply an exciting new recovery technology to this process. Previously, attempts to separate the nickel residue and acid bath had proven far too costly. As a result, the acid and metal by products from acid etch solutions became hazardous waste, and required extensive and labor intensive disposal. The new technology combines simple, proven distillation techniques with advanced corrosion resistant materials. The resulting system reduces raw material and waste disposal costs while providing a clean, reusable acid solution. The process extends bath useful life, significantly reduces production costs while improving process quality. As if this alone were not good enough, waste acid has been reduced by 25,000 gallons/yr.

• Environmentally Acceptable Strippers: The use of an alternative chemical striper in place of Methylene Chloride and Phenol resulted in a reduction of over 500,000 lbs/yr of toxics. Tinker prototyped and selected an alternative two part stripper with a benzyl alcohol bas. This new chemical means that workers have a significantly reduced exposure to the know carcinogen-methylene chloride.



Stripping of KC-135 Aircraft using EA strippers

• **Dual Wire Arc**: A Dual wire arc process is being used to apply multiple metal coatings as a buildup repair for jet engine parts. A high voltage arc is struck between oppositely charged wires. Simultaneously, compressed air is forced through a gap between the ends of each wire. The force of the compressed air stream suspends and carries the molten drops of metal, hurling them against the surface to be plated. This builds up a useable layer of metal. The old process of dipping parts in a chromium and nickel solution was much slower and even more hazardous. Savings of some \$89K per year have been realized by implementing this technology.



Twin Wire Flame Spray

An aggressive environmental program at TAFB has set the standard for defense installations everywhere. Tinker is poised for making the 21st century a success with newer better technologies to even further reduce dependence and use of toxic chemical.

Productivity Improvements With a New Vapor Degreasing Cleaning Process At Williams International

Roger Evans, Williams International; & John Hoffman & B. Carroll Smiley, Petroferm, Inc., Fernandina Beach, FL

Williams International, a manufacturer of jet engines for the military in applications, such as cruise missiles, and civilian markets, with engines such as the new EJ-22 turbofan engine, has implemented a new cleaning process. This paper will explore the decision-making process that manufacturing personnel used in selecting vapor degreasing with a normal propyl bromide (nPB)/isopropyl alcohol (IPA) azeotrope. The significant increase in productivity that the new cleaning process has produced over the old aqueous cleaning process will be explored, as will details of the operation and maintenance of the new system.

Paper not available

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Insights Regarding the Adhesion Mechanism for Supplementary Organic Coatings on Porous Anodic Films

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Abstract: A novel anodic coating process for aluminum and aluminum alloy substrates has been developed that enables the formation of composite polymer-metal oxide films. An extensive study comparing the adhesion of various inks and adhesives to the new finish and to Types I, II and III anodic films elucidates the reaction and bonding mechanism of the supplementary coatings. By understanding this mechanism, a basis for organic-inorganic reactions within anodic films can be realized, resulting in higher reliability attachments and offering new areas for finish application.

1. Introduction

The use of dual phase transition layers to facilitate ceramic to metal bonding is a welldeveloped, reliable technology that has a long history of application in any industry that employs seals.^{1, 2} In the realm of polymer – metal sealing, there is currently no known true transition layer. Mechanical and/or chemical roughening and chemical adhesion promoters such as primers are often utilized to enable adhesion of a polymer layer to a metal substrate, be it an ink, paint, lacquer or adhesive. On aluminum, the surface is often anodized.

Anodizing can be viewed as the deliberate, electrochemically controlled corrosion of the aluminum surface in aqueous solutions of sulfuric, chromic or oxalic acid.³ The resultant films are uniform, continuous and exhibit a unique porous, columnar structure. See Figure no. 1.

Thin chromic acid (Type I) and sulfuric acid (Type II) anodic finishes are often dyed, laminated, and/or used as a primer layer for paint. Thin polymer dispersion layers of colloidal PTFE are applied to the surface of hard anodized (Type III) films to reduce friction and increase surface smoothness as an enhancement to the inherent hardness of a Type III anodic finish, often utilized in wear and abrasion applications. Similarities between the aluminum anodization process and the oxidative polymerization reactions for certain conjugated polymers, as well as the electroactive characteristics of these polymers with protonic acid doping indicated anodizing and electrodeposition of the polymer could be carried out simultaneously. producing composite polymer-metal oxide films. Uniform, continuous films have been electrochemically formed which exhibit structural modification and polymer phase inclusion.

To date, engineering testing of the composite finish has shown increased dyeability, UV stability and adhesion of subsequent polymer layers. Testing has been performed in the laboratory and in various field applications. In an effort to understand the performance improvements, comparative scientific characterization of the composite finish has been performed to standard anodic finishes.

2. Engineering Characterization

A. Color Fastness

The South Florida Test Service performed accelerated weathering tests according to MIL A 8625 F modifications to ASTM G 23. Aluminum alloy 6061 T6 panels were anodized both conventionally (Type II) and with the composite finish, both dyed black and sealed. Specific panel color, quantifying both the hue and brightness, was determined with a Hunterlab Ultrascan spectrocolorimeter. The panels were then exposed to 200 hours of radiation using an Atlas FDA-R Single Enclosed Carbon Arc Fade-Ometer. Differences in color were then quantified by the spectrocolorimeter, outlining the color change over time.

The reported summation of all color and brightness changes for the anodized composite finish, the coefficient value E^* , was 0.42, one third of the change exhibited by the 1.45 E value for the conventionally anodized (Type II) panel.

B. Adhesion Testing

Two hundred (200) samples each of aluminum alloy 6061 components were finished with a hard version of the composite coating (Type III equivalent), dyed black and sealed two different ways. One set of one hundred (100) components was sealed with hot water and one set of one hundred components was sealed in a duplex fashion. first with nickel acetate and followed by a sodium dichromate seal. The sample sets were subjected to four (4) permutations of cleaning and treatment with an adhesion promoter: no cleaning with no bonding agent, cleaned with no bonding agent, no cleaning with bonding agent, and cleaned with bonding agent. All were coated with adhesive and over-molded with a rubberbased form.

Adhesion testing of the samples was based in ASTM B571"Test Methods for Adhesion of Metallic Coatings", paragraph 11, and "Peel Test". The rubber coating was cut and pulled at an angle of 90° to the surface of the piece with efforts to maintain the rate of pull. Following testing, the delaminated surfaces were evaluated to determine the point of failure. Inadequate adhesion was considered as failure in the coatingsubstrate interface.

Comparison of the various samples determined that there was little difference in adhesion between the samples processed with the hot water seal and those with the duplex seal. In fact, it was found that the degreasing operation performed prior to treatment with the adhesion promoter could successfully be eliminated without compromising adhesion of the rubber form.

3. Scientific Characterization

A. Transmission Electron Microscopy

Unsealed 10 cm² panels of aluminum alloy 6061 were finished with the composite coating, a conventional Type II anodic finish and a chromic acid (Type I) anodic finish. The average finish thickness of the samples from each group was 4 to 5 microns. The panels were screen printed with a cellulose-based ink commonly used in the anodizing industry.

Thin-sectioned samples of a conventional Type II anodized and screen-printed panel, a composite finished and screen-printed panel and a chromic acid finished and screen printed panel were prepared for examination by TEM. Epoxy was used to mount and fix the samples during It was noted that the preparation. conventional Type II samples exhibited extraction of the ink into the epoxy bond line. The composite samples exhibited no evidence of extraction whatsoever. Clearly, more retention of the ink in the presence of an extracting agent, suggests the screen print ink was better bonded to the composite finish or at minimum, the composite finish is more polar than the Type II finish.

Examination within the TEM revealed the ink components (pigments, cellulose-based resin) exhibited segregation. The ink layer the Type II sample measured on approximately 50 nm thick. The ink layer was separate and distinct from the surface of the anodic film. Intrusion of the ink within the pores of the film was limited to one small area, to a depth of approximately 10nm. The pigment particles appeared fairly uniform in size and shape with evidence of agglomeration. The resin appeared amorphous. See figure no. 2.

Examination of the screen-printed composite finish revealed the quality of the ink layer was very different between the samples, suggesting the solvent permanency may have had an effect on the preparation. However, the interface between the ink and composite film surface exhibited what appeared to be interaction with the composite film microstructure for a distance of approximately 10 - 40 nm. EDS analysis of across the interface determined the constituents of ink within this region of the composite coating. See figure no. 3.

B. High Intensity Infrared (FT-IR) Spectrographic Analysis

TEM sections of a Type II unsealed anodic film and composite films were analyzed by way of high intensity Fourier Transform Infrared Spectrographic analysis. The energy source for the instrument was hooked up to a synchrotron light source. The resolution of the instrument was $4 - 5 \mu$.

Sections of each coating were analyzed using a 4μ X 30μ aperture. Data was collected from the aluminum-anodic film interface (bottom), the film center and the top. The films measured 20-25 μ thick.

The trends in the infrared data collected from the bottom of the films to the top strongly suggest a shift in the formation and amount of active hydroxide and sulfate groups. The Al-O feature at approximately 750 cm⁻¹ dominates, but shifts upward in the spectra as the sulfate peaks at 1000 to 1100 cm⁻¹ become larger and more defined. With the development of the sulfate absorption, hydroxide absorption becomes pronounced. This actually makes sense, as the surface of the anodic film regardless of Type or formulation, should exhibit more hydration.

The composite coating exhibited evidence of inclusion of the electroactive modifier with absorption in the higher IR. The spectral shifts toward the higher IR were noted from the substrate, where the inorganic absorbances were most pronounced to the middle and finally the surface portions where absorption of both OH^1 and carbon-based inorganic salts were detected within the composite film. See figure nos. 4 and 5.

In order to identify the molecular species of the oxide as formed during conventional anodization, a hot water sealed Type III coating was processed within argon plasma. With increased exposure time within the plasma, a residue developed on the surface of the coating. Infrared analysis of the residue determined absorption characteristics for hydrated aluminum sulfate and/or aluminite: $AI_2(SO_4) \cdot 18H_2O$ and/or $AI_2(SO_4)(OH)_{4} \cdot 7H_2O$.

These results indicate the presence of a compositional gradient from the substrate to the finish surface. This shows that the portions of the film that remain in contact with the electrolyte, in addition to hydration, will also adsorb active counter ion species from the electrolyte. Since the central pore is in constant contact with the electrolyte, a compositional and therefore reactivity gradient across the porous structure will also be formed, hence the ability of the film to be modified through additives to the electrolyte.

C. X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) studies were performed on Type II and on two (2) groups of composite anodized samples. The composite samples were exposed to different anodizing times. One group of samples was representative of the typical exposure time of 60 minutes and the other group was representative of an extended exposure time. The samples were anodized and mechanically removed to sealed containers to prevent surface contamination through handling or by ambient air. This insured the analysis results would reflect the actual anodized surface composition from a depth of 0 to 30 Angstroms.

The Type II and composite samples anodized for the typical exposure time exhibited the presence of sulfur as sulfate. Additional oxygen and aluminum was also The high-level binding energy detected. component for oxygen corresponded to H_0O and OH, which supported the infrared data. The aluminum detected in the film surface of these samples was not metallic in nature; the low binding energy component was typical for disordered aluminum oxide. The composite sample did show chemical inclusion of the electroactive modifier. Saturated and _-conjugated carbons were noted with distinct linkages to the disordered (hvdr)oxide structure as HO-C=O. O-C=O and C-OH.

XPS analysis of the extended exposure samples determined strikingly different surface constituents. More of the electroactive additive was detected in the surface of these samples. No sulfur was determined. Evidence of metallic aluminum, and copper, as Cu₂O was also identified. The results were important because they indicated these species were actually deposited from the electrolyte and not a function of the anodization of the substrate.

4. Discussion

Comparative engineering testing by way of light fastness. adhesion and dve permanency testing was performed on samples finished with standard Type I, II, and III anodized finishes and samples finished with a new composite anodic finish for aluminum. Testing determined differences in performance between the two finishes. Comparative scientific characterization of the finishes was also performed.

Comparative analysis within the TEM determined the microstructure of the composite film appeared finer and denser. The ink-finish interface exhibited evidence of interaction between the ink layer and the finish microstructure within the first 40 nm of the composite finish. EDS across the interface revealed the presence of chlorine. a constituent of the ink, not characteristic for the composite anodizing process. The Type II film exhibited a less dense microstructure with the unidirectional columns typical for anodic structures. The ink-finish interface was clearly delineated with evidence of delamination; no intrusion of the ink within the porous structure was noted. These results strongly indicate the ink and the composite film indeed reacted together, producing a well-bonded interface.

High Intensity FT-IR analysis determined that in addition to the microstructural gradient, a compositional gradient existed from the substrate to the composite finish surface. Aluminum oxide and sulfate species were identified throughout the finish thickness while carbon-based inorganic salts were detected within the top 4-5 microns of the composite finish.

The XPS results show conclusively the inclusion of fragments of the electroactive polymer modifier. Saturated and conjugated carbons were noted. Probably the most significant ligands determined, regarding the possibility of functionality and therefore bonding to subsequent polymers. were carbonyl linkages, bound to the disordered (hydr)oxide structure. The C=O and -COOH groups are powerful electronwithdrawing groups, and therefore would be expected to react with subsequent polymer additions through electrophilic addition. forming stable intermediate compounds between the composite finish and the paint, adhesive, or any other polymer layer.⁴⁻¹

Improved light fastness of the composite finish by a factor of three over samples with a standard Type II anodic finish was determined. These results are believed to be the result of the modification of the anodic finish microstructure introduced through the addition of the electroactive polymer to the anodizing electrolyte. The more cellular structure would result in scattering of light within the finish, rather than direct reflection as would be the case with the unidirectional columns of the typical Type II microstructure. Direct reflection would tend to degrade the dye molecules through photoinitiated oxidation. Another possibility to consider would be that the retained polymeric ligands might bind with the dve, improving the stability of the color within the finish.

Upon consideration of the adhesion testing results, use of the composite finish as a stand-alone finish, hot water sealed, was selected. Adhesion of the bonding agent was as good to the composite finish as it was to the dichromate seal. Implementation of the composite finish with the hot water seal eliminated the use of the heavy metal seal, and the degreasing process, therefore promoting a more environmentally friendly finish and process. It also saved time and money through the elimination of the degreasing step and the duplex sealing process all together.

5. Conclusion

The results of the engineering tests and the indications of the scientific characterization strongly suggest the composite coating, because of the retention of the organic ligands, is a better binding surface for subsequent polymer layers. The composite finish therefore offers the first true transition layer that enables actual chemical polymer-metal bonding. Additional research and analysis is being performed to confirm these results.

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Figure 1a: TEM photomicrograph of a conventional Type II anodic film microstructure.



Figure 1b: TEM photomicrograph of a conventional Type III anodic film microstructure.



Figure 2: TEM photomicrograph of Type II finish with screen-printed ink layer. Note delamination at ink-finish interface.



Figure 3: TEM photomicrograph of composite finish with screen-printed ink layer. Note apparent interaction at ink-finish interface.



Figure 4: IR spectrum of composite anodic film adjacent to the aluminum substrate is identical to a conventionally anodized Type II film. The low-end absorbance is typical for inorganic species



Figure 5: IR spectrum of modified composite film exhibits a shift in the inorganic spectrum toward the more chemically reactive species of sulfate and hydroxide. Some organic absorbances are also present indicative of additive inclusion.

Recycling Wax: What are the Benefits?

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Most airline plating facilities use wax to mask off engine and landing gear components. This prevents plating and/or chemical etching from occurring on areas not requiring plating. As a general observation in most facilities, the wax tank used for masking a part to be chrome plated is also used to remove the bulk of wax from the parts being processed. The same holds true for nickel plating. The wax build-up and removal takes place in the same wax tank. This is done to prevent cross-contamination between the chrome and nickel baths. Over the past 35 years, UAL has used hot water to remove wax. It recycles its wax by removing the wax in a hot water tank that rinses the chemicals out of the wax. The wax floats to the top of the tank and overflows into a drain leading to another tank. UAL has four wax tanks with a total wax content of 47,245 lb. In 1999, we disposed of 1,250 lb of solid, unusable wax at a cost of \$2,625.00. This cost is far less than disposing of the contents or partial contents of the wax tanks, then replenishing with new wax each year. This paper will explain the method we use to recycle wax, the flow of wax in the recycling process, the design of the tanks, the hazards and concerns in the recycling process, and the benefits of in-house recycling.

Paper not available

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A Step-by-step Approach for Specifying & Designing an Engine Overhaul Cleaning System

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When it comes to cleaning engine components, there are many issues that are unique to the aerospace industry: part size, exotic base metals, traceability requirements, aggressive chemistries and the high cost of components, just to name a few. This paper addresses these issues and helps form a guide so that an informed decision can be made when purchasing a new engine-cleaning line or upgrading and improving an existing line. Discussions are included on methods of agitation, spray versus immersion cleaning, material handling options, waste reduction methods and process control issues.

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Overview

As the aerospace industry rapidly changes, overhaul and maintenance facilities need to respond accordingly. Trends in the industry such as increasingly larger aircraft and the need to have tighter process control have forced overhaul facilities to reassess their capabilities and make changes to accommodate the new requirements.

During the engine overhaul process, most engine components require cleaning, even before they can be inspected. Then, after inspection and NDT (nondestructive testing), they may require secondary cleaning. This makes cleaning an intricate part of the engine overhaul procedure. Unless an engine overhaul facility's cleaning is being outsourced, it will have some degree of cleaning capacity.

This paper looks at some of the trends in the industry that may require engine-cleaning lines to be updated or improved. It also touches on some issues that are unique to the industry and require special attention when specifying and designing an engine overhaul line. In addition, it will help provide a basic guideline on some key issues to be considered when making a decision of this magnitude.

Industry Trends

Recent trends in the aerospace industry have prompted engine overhaul and maintenance facilities worldwide to review, update and modify their engine processing and cleaning equipment.

Larger Engine Components

With the advent of larger aircraft, come larger engines and engine components. Existing processing/cleaning systems are being stretched to their limits to accommodate these components. When these process tanks were initially designed, no one would have envisioned that they would one day need to process engines nearly as large in diameter as the entire fuselage of many commercial jet airliners.

Improved Cleaning Methods

Process tanks, commonly referred to as "soak tanks," are more frequently than not, simply large tanks for soaking the engine components. Some systems may incorporate some means of filtration that will introduce some solution movement in the tank, but

the actual cleaning is taking place by combining the cleaning chemical action with heat over a specified period of time. An existing cleaning system, which utilizes the "soak method," can be greatly improved by introducing some form of mechanical energy into the process tank. Common forms of agitation are solution agitation, part movement through the solution, or ultrasonic energy. This energy not only improves the cleaning results, but also can greatly reduce the overall cleaning time.

The Reduction and Elimination of Solvent Cleaning New environmental regulations on certain base solvents have required overhaul facilities to look for new ways of cleaning without solvent-based cleaners.

Example: A common method to clean engine bearings has always been to soak the bearings in a solvent-based cleaning solution. These solvents are very effective at removing the carbon, grease and oils, which are the typical contaminates on an engine bearing. The engine manufactures have updated the cleaning specifications to include procedures that utilize aqueous-based cleaning solutions, with a series of water rinses and a water-displacing oil step. What was once a single-step soak process, is now a three-to-four step process. Pratt & Whitney's SPOP 216 is an example of just such a procedure.¹

Cleaning times of several hours were quite common in this bearing-cleaning example, when using solvents. The new aqueous methods have improved the cleaning, while significantly reducing the cleaning time. Some bearings, which used to require up to eight hours in a solvent cleaner, are being cleaned in the aqueous process in less than 30 minutes.²

Increased Process Control and Part Traceability A much greater emphasis is being placed on tighter, more accurate process control of the cleaning system's temperature, cycle times, chemical concentrations and rinse water purity. By ensuring that these parameters are in the optimal ranges, the final cleaning results can be maximized.

As an engine is disassembled, its components are closely tracked throughout the entire overhaul process. Detailed records are kept during tear down, NDT and reassemble. One area of record keeping and traceablility in the engine overhaul process that needs improvement is the cleaning phase. With manual transfer systems and outdated control systems, the data being collected usually falls short in quality and quantity compared to what is currently available with today's technology. New control systems and software have the capability to track a hundred or more data inputs per process batch. What was once just a basic log for documenting when a part was cleaned and through what procedure, can now include precise cycle times, temperatures, drip times and transfer times, to name a few.

Cellular Cleaning

Many overhaul shops are investigating the feasibility of moving from a single large central cleaning line, where all components flow through, to independent cellular cleaning systems within a given work cell or component area. This reduces the load on the central cleaning line, brings the control back to the cell and usually reduces costs (in time and dollars) associated with in-process material handling.

This sounds like a great concept. However, it is simply not practical for every application and can be extremely cost prohibitive. For example, an APU's (Auxiliary Power Unit) cleaning requirements and procedures are very comparable to other much larger engine components such as an engine gearbox housing. There are many steps and the number of process tanks required can be numerous. In this example, most of the processing stages in the gearbox line would need to be duplicated in the APU work cell to have true independent cellular cleaning overhaul.

Cleaning Issues Unique to the Aerospace Industry

The aerospace industry is very unique in every aspect. This also holds true when discussing issues specific to aircraft engine overhaul.

Large and Variable Part Size

Overhaul facilities need to be extremely flexible when it comes to component part size. As passenger and military aircraft grow in size, everything from hangers, jetways and cleaning capacities/capabilities need to increase in size accordingly. As major assemblies are broken down into their smaller components, the overhaul shop has to have the flexibility to process extremely large parts, as well as small components such as turbine blades and fittings.

Exotic Materials

High operating temperatures combined with high stress loads and lightweight requirements are a few factors that require many engine components to be designed using exotic metals and alloys that are unique to the aerospace industry. While these metals are soiled with build-up that requires very aggressive chemicals, they also require unique cleaning chemistries so as not to damage their integrity.

Component Cost

The cost of the materials of construction combined with the OEM manufacturing costs and the liabilities which follow the part throughout it's operating life, correlate to engine components with extraordinary price tags. A single engine bearing can cost \$50,000 or more. For this reason, it is imperative that process times and material handling techniques are closely monitored. For the costs associated with one damaged or scrapped part, a buyer could purchase a new cellular cleaning line.

Because of these high dollar values, reducing engine overhaul turnaround time has a significant and direct effect on the bottom line. Faster turnaround time results in reduced inventory requirements, in entire engines and spare parts. Increasing the efficiency and speed of cleaning in the overhaul process will indirectly equate to significant cost savings. With commercial engine costing exceeding \$12,000,000 or more, one can see how much potential cost savings exists.

Traceability

Part traceability is pertinent in engine overhaul. As the components are broken down into smaller components, they are cleaned and inspected. All of these procedures are well documented and follow the part throughout its operating life. More of an emphasis is currently being placed on better record keeping and traceability of a part's cleaning history. In a high profile case, 8,200 engine blades that were improperly cleaned were recalled. It was found that an improper cleaning process caused fatigue cracks in the blades. Because of the high degree of traceability, the actual day that the blades were cleaned was identified and notices were sent to all airlines affected. As a result, new procedures and regulations have been implemented for cleaning this engine component.³

Basic Cleaning Formula

When designing or upgrading a cleaning system, it is helpful to understand the basics of the Cleaning Formula. The four factors of the Cleaning Formula are: time, temperature, chemistry/concentration and the method of cleaning. Common methods of cleaning include, spray, soak, hand wipe and immersion agitation. When one of these factors is changed, it has a direct and sometimes exponential effect on the others.

Time

Tank time is usually one of the first variables to be set. Typical cleaning times can range from 2 minutes to upwards of 30 minutes. Reducing the cleaning time can increase the cleaning system's volume capacity. However, there are strict guidelines that are provided by the engine OEM detailing these parameters. These are typically referred to as overhaul standard practices. In the case of Pratt & Whitney, they use the term "SPOP."

These "practices" are more than just guidelines. Exposing a part to some of the cleaning chemicals for an extended period of time can be detrimental to the part's integrity. For this reason, it is quite common to have maximum cleaning cycle time specifications.

The overall process time, which includes cleaning, rinsing and secondary chemical applications is the period of time the part is in process from loading to unloading. The total time is usually dictated by the initial cleaning cycle time, which tends to have the longest wet process time requirement. If the system incorporates a forced air drying stage, depending on the part configuration or the number of parts in a process batch, this could also be the "bottleneck" in the overall process time.

Temperature

The manufactures of the cleaning compounds recommend operating temperatures. These are

specific to each product, as they are frequently formulated with surfactants or a combination of surfactants, which are most effective in certain temperature ranges.

An increase in temperature usually will have a direct effect on the cycle time and can reduce the required chemical concentrations. Too much of an increase (over the recommended operating temperature) can have an adverse effect on the cleaning chemistry and can actually "split out" the surfactants in the cleaners, leaving the bath "dead." Depending on the formula, the bath may or may not be able to be revived by lowering the temperature back to the recommended operating range and mixing the solution.

Chemistry/Concentrations

A significant percentage of cleaning chemicals used in engine overhaul applications are water-based. Their recommended concentrations can range from 5% to 50%. In general, cleaning in a 5% to 10% concentration range is quite common. In more aggressive applications, such as those using permanganate-based cleaners, percentages of 40% to 50% concentrations are quite common. Again, the cleaning chemical manufacturer specifies these ranges.

In addition, the engine OEM has its recommended ranges that may differ slightly from the data sheet provided by the cleaning chemical supplier. Please note that in most aerospace cleaning applications, the engine OEM not only has recommended operating times, temperatures and concentrations, but they also have a list of approved products. If the product is not on the approved list, it cannot be used in the cleaning line.

Method of Cleaning or Mechanical Energy

Due to the complex geometries of numerous engine components, the most common form of cleaning is to immerse the part in a cleaning solution. Other methods of cleaning such as spraying or hand wiping can be and may need to be incorporated into the cleaning process. For purposes of discussion, this paper is limited to immersion cleaning, as it represents the most common method used in a typical engine overhaul facility. Large soak tanks, which are quite common in the plating industry, are also quite common in engine overhaul facilities and are frequently used as cleaning tanks. By introducing some form of mechanical energy into the process tanks, the cleaning results can be improved and cycle times reduced. When specifying the method of introducing mechanical energy into the cleaning process, the engine OEM standard practices manuals may provide several options with no preferred method. This enables the overhaul facility the flexibility to choose the preferred method, specific to their needs.

There are basically three methods of creating mechanical energy in a cleaning tank: liquid agitation, part agitation through the solution and ultrasonics. All three will be discussed in greater detail in the next section of this paper.

Designing a New Cleaning Line

When designing a new cleaning system from the ground up, several factors need to be addressed.

Number of Process Tanks

If the operation requires overhauling of a single manufacturer's engine or engines, then determining the number of process stages is simplified. The OEM will have recommended procedures, which will dictate how many process stages are required. You may have the flexibility to add a second wash stage or extra rinses, but rarely can you eliminate a stage or step.

When reviewing recommended process times, you most likely will note that there are one or two steps that require significantly more process time than the other steps. If this time requirement is seen as a potential volume limitation for the cleaning system, a second or even a third stage maybe justifiable. For example, if one stage requires 30 minutes and the others are 15 minutes or less, by adding a duplicate stage, the limiting process time can be reduced to two steps of 15 minutes. The total process time of 30 minutes is still met, yet the volume capacity of the system has doubled for the cost of one more process tank.

If your overhaul facility processes engines from different manufacturers, you will need to design a hybrid system, or have a cleaning line for each style/type of engine. Dedicated cleaning lines are not always practical for obvious reasons.

It is quite probable that each manufacturer will have slightly different procedures and approved cleaning chemicals. The goal would be to find as many shared similarities, so as to reduce the total number of process stages required. There tends to be a great deal of overlap between different manufacturer's procedures.

When reviewing the OEM standard practices and procedures, it is likely that some of the cleaners have been approved by more than one engine manufacturer. By specifying products that have the widest range of approvals, the number of process tanks can be minimized. If the process tanks cannot be "shared," or if it is preferred to have dedicated cleaners, then it will be necessary to have dedicated tanks for each individual supplier's requirements.

If recommended times and temperatures overlap, an internal operating range can be written which incorporates only the overlapping ranges. The most significant range is the upper operating temperature limitation. If one manufacture has a slightly lower maximum operating temperature for the same cleaning solution, the procedure can be written with the lower temperature for both applications. The same concept holds true for the recommended chemical concentration parameters.

You will also have some flexibility when specifying the number of rinse tanks. Some procedures may have a minimum requirement, but rarely will you see a maximum requirement. It is quite common to have at least one rinse stage between chemical stages, with one or more rinses for the final rinsing. Keep in mind, your parts will only be as clean as your final rinse.

One simple method of waste reduction or minimization is to have a series of two or more final rinse tanks counterflowing. This not only reduces rinse water usage, but also helps to ensure a cleaner final product. This theory holds true whether the process incorporates treated water or tap water.

Table	1:	Water	Req	uired	to	Dilute	One	Gallon	of	Dragout ⁴	ŀ
										0	

Dilution	One Rinse	Counterflowing Rinses					
Ratio	(gal)	2	3	4	5		
100:1	99	10.0	4.3	3.0	2.3		
1,000:1	999	31.0	10.1	5.4	3.8		
5,000:1	4,999	70.0	17.0	8.2	5.3		
10,000:1	9,999	100.0	21.0	10.0	6.1		
20,000:1	19,999	141.0	27.0	12.0	7.0		

For two gallons of dragout, multiply water figures by two, for 1/2 gallon multiply by 0.5 etc.

Sizing Process Stages

The process tank size is directly related to the maximum part size to be processed in the tank, in the orientation that promotes the best cleaning. Some parts will clean better in a particular orientation.

First, determine the maximum part size to be processed and the "envelope" it occupies in the desired orientation. This will dictate the maximum basket or carrier size to be used for material handling. Second, there will be minimum recommended tank clearances, space for ancillary equipment and a desired liquid level above the part during processing. This will give you a baseline for starting. Each individual cleaning system manufacturer will have their own requirements and recommendations, specific to their equipment.

One basic principle commonly used in the cleaning industry is the 80/20 rule. To apply this rule to this application, one must first closely review the mix of parts and the range of sizes. If a very small percentage of the parts are much larger than the majority, it may be more practical and cost effective to design the system's size around the larger percentage of parts. The larger parts could then be cleaned with alternative means such as hand scrubbing or spraying.

Materials of Construction

Due to the aggressive nature of the cleaning chemicals and the high operating temperatures utilized in an engine overhaul application, highly chemical resistant materials of construction are required. The most common is 304 stainless steel. The chemical supplier may recommend other series of stainless such as 316. It is common to have the support structure fabricated out of mild steel with a chemical resistant paint and all wetted parts fabricated in the recommended stainless steel series.

One design feature to consider, is to specify that all support structures that come in contact with the floor, should be fabricated out of a series of stainless steel. It is inevitable that chemicals will come in contact with the support structures and over time, may have a detrimental effect on the integrity of the process tanks. If a stainless steel base is designed into the support structure, these chemicals can be periodically rinsed down without any ill effect on the tanks. This also helps facilitate a safe and clean working environment.

One other common method to make the process tanks more chemical resistant is to line them with a chemical resistant material such as polypropylene. If an alternative material is considered for liners, consider not only its chemical resistance characteristics, but also its temperature limitations.

A major airline overhaul and maintenance facility currently has process tanks that are fabricated out of ¹/₄ inch plate, 304 stainless steel. They have been in operation for close to thirty years. Due to the integrity of the tank itself, these process tanks, with a little refurbishing, could quite conceivably last another 30 years.

Method of Agitation

If you have an existing system utilizing simple soaking process tanks, the addition of agitation will greatly enhance the cleaning results and reduce the average cleaning cycle time. If you are starting from square one with a new process line, there are three basic methods to consider. If you were attempting to modify your existing process tanks, not all methods would be practical without significantly reducing the working envelope of the system.

Liquid agitation is one of the least costly methods, especially if it is a retrofit for an existing cleaning line. The most simplistic form is a circulation pump, which will create liquid movement in the tank. This method can be greatly improved upon by using a series of eductors connected to a manifold header. The eductors enable smaller pumps to circulate large volumes of tank solution. Due to their venturi design, they can have a circulation rate of four to five times the pump rate.⁵ This greatly increases the mechanical energy, thereby increasing the cleaning action. If these eductors are mounted on ball joints, they can be positioned in such a way to create an efficient circulation pattern or a whirlpool-like effect.

Theory Behind Eductor Agitation



When specifying the actual pump size, the materials of construction and the flow rate, one must first consider the aggressive nature of the cleaning chemicals. As with the tank construction, the pump will need to be highly chemical resistant. In addition, its seals will need to compatible with the solutions. One way to ensure that the seals are compatible, is to eliminate them altogether with a seal-less vertical pump design. This not only eliminates the seal, but also reduces the amount of external plumbing and therefore, the potential for leakage at pipe joints and unions.

The flow rate requirement is very subjective. If the tanks are already existing soak tanks that are being retrofitted, any flow rate will be an improvement. When specifying the pump flow rate for a new process tank, it needs to be enough to enhance the cleaning but not so much that it creates the potential for part damage. Several turnovers of the solution per hour are recommended for best results.

Vertical part agitation is also an efficient method to introduce mechanical agitation in the solution tank. By moving the part through the solution, you create a scrubbing action that is very effective at removing soils. In addition, this method is very effective at ensuring that the intricate part configurations are thoroughly drained and flushed numerous times in the cleaning cycle. When designing a system with vertical part agitation it is highly recommended that all mechanical parts, such as a pneumatic or hydraulic cylinders, do not come in direct contact with the aggressive chemicals. This will reduce the required maintenance and extend the system's operating life. If properly designed, vertical part agitation systems are very dependable and will last for years or even decades.

In addition, insist on a method of part agitation that enables you to control both the speed of the agitation (the frequency of stroke), as well as the length of stroke. Some part configurations clean better at different stroke lengths and some parts may be damaged if the stroke speed/frequency is too aggressive.

Another type of agitation that is an option, is ultrasonic energy. Ultrasonic transducers operate at a high-frequency range above the upper range of human hearing. In aerospace applications, operating frequencies between 20 kHz and 40 kHz are quite common and effective.

Ultrasonic pressure waves propagate through the solution causing alternating high and low pressure areas at the part surface. The low pressure causes a cavitation bubble to occur. The high pressure then causes the bubble to implode. Temperatures inside the cavitation bubble can reach 5,482 °C (9,900°F) with pressures up to 500 atm. The implosion event creates a jet stream that travels up to 400 km/hr.⁶ The combination of pressure, velocity and temperature create very effective cleaning energy.

When specifying the ultrasonic frequency, it is best to consult the experts. They will need to know details such as part size, weight, cleaning solution, soils and base metals.

Determining how many watts/liter of ultrasonics are needed can end up being a budgeting factor. In aerospace applications, it is possible to have process tank volumes in excess of 7,500 liters (\approx 2,000 gallons) and operating ranges of 2.6-4.0 watts/liter (\approx 10-15 watts/gallon) are quite common. Factoring in a very conservative cost of \$5/watt and a single 7,500 liter tank, fitted with 19,500 watts (2.6 watts/liter) of ultrasonics, will cost \$97,500.

If the process tanks are existing soak tanks and they are being upgraded with a form of agitation, certain styles/types of ultrasonics are designed as drop-in retrofit units. In addition to the ease of installation, they also are low profile and do not require a great deal of space, so the tank's working envelope size may not be compromised. The ultrasonic supplier should review the tank design to determine the ultrasonic installation location that will provide the greatest cleaning effectiveness.

It is important to note that the process tanks that are retrofitted with ultrasonics must be fabricated out of stainless steel, because over time, mild steel will not hold up to the aggressive nature of the ultrasonic cavitation bubbles' scrubbing action.

The engine manufacture's standard practices and procedures of cleaning for particular components may dictate ultrasonic power, frequency and time limitations. For example, GE Aircraft Engines' Standard Practices Manual on engine bearing cleaning is very specific on time limitations for cleaning with ultrasonics. In section 70-22-01, dated November 1997, it states, "ultrasonic agitation is allowed for only one five minute interval for each bearing cleaning cycle."⁷

Pratt & Whitney's SPOP 216 has similar requirements on the frequency and the total wattage of optional ultrasonics. "A 20 or 40 kHz frequency ultrasonic unit is recommended with an intensity of 6-11 watts/square inch."⁸

Method of Heating and Heat Requirements

Not all of the process tanks will require heat. For those that do, they may have operating ranges between 50°C and 94°C (\approx 120°F-200°F). A common mistake is under-sizing the watt (BTU) capacity of the heating system. When specifying the watt (BTU) requirements, factor in:

- Tank volume
- Operating temperature requirements
- Anticipated kgs./lbs. product per hour
- Type of metals being processed
- Temperature of incoming parts
- Heat loss due to evaporation
- Desired heat up times
- Make up water temperature and volume/hour
- Plant humidity
- Velocity of air across the tank (exhaust system)

- Ambient air temperature
- Tank insulation value

Steam, gas and electricity are the most common methods to heat process tank solutions. The method chosen is usually made based on usage costs, availability and the corrosive characteristics of the solution.

A large percentage of overhaul shops are equipped with central steam. Therefore, steam heated engine cleaning lines tend to be the most common. Steam coils are made of pipe embossed metal plates with steam passages as the heat transfer surface. With steam heat coils, the heat can be spread out over a large surface area. This is referred to as "low heat flux density," which is the amount of heat transferred per unit area of the heating surface. Low heat flux density (also known as low watt density) is desirable, as it reduces the frequency in which the steam coils need to be cleaned and the tank has a limited maximum input temperature (i.e. maximum steam inlet temperature). In addition, they can be designed in such a way that they can be easily removed for routine cleaning and maintenance and they allow for a great deal of flexibility in shape and size to fit a variety of tank requirements. The disadvantages are the requirement for a boiler system, steam and condensate piping and the efficiency of the steamheated systems will vary depending on the type of boiler and steam system selected.

When specifying the materials of construction for the steam coils, factor in which chemicals will be used in the process tank. Stainless steel 316 series is recommended for all steam coils and for some chemical solutions, more corrosive resistant materials and exotic metals maybe warranted.

Gas heat is probably the second most common form of heating for these applications. Gas, usually natural or propane, is burned in a chamber or immersion gas coil. The efficiency of the heating is based upon the firing rate of the burner and the length of the gas coil. Maximum efficiencies are usually about 80% (above 80% there will be condensation in the gas coil). The heat flux density can vary depending on the surface area of the gas coil and the firing rate. Some of the newer pressurized burner systems are capable of firing into small diameter gas coils and achieving very high heat transfer rates (high heat flux density) especially near the burner entrance where the gas temperature is the highest.

If the gas tube gets fouled and the heat transfer is restricted, the temperature of the heat transfer surface will rise and the efficiency of the heater will go down (flue gas temperature will increase). With high heat flux densities, the burner tube may be damaged or burn out as a result of fouling. Gas burner controls should be specified based on insurance carrier requirements and local codes.

The advantage of gas, in some case, is lower fuel costs and possibly low heat flux density. Disadvantages are lower efficiency than electric heat, the need to vent combustion gasses and burn out potential.

Probably the least common method to heat a large process tank is electrically. In an electric system, an electric current is passed through a resistance element resulting in heat. The heat is conducted through a sheath material that separates the resistive heating element from the solution. A contactor controls the flow of electric power to the heating element in response to tank temperature and set point. Electric heaters are made in a variety of watt densities and sheath materials. Unlike steam, the maximum heater temperature is not limited to the nature of the energy supply. The electric heater will supply a constant amount of heat. If the heat transfer is restricted, the temperature of the heat transfer surface will be forced up until the heat does transfer or until the heater burns out due to over temperature.

The advantages of electric heat are the relatively small size, easy installation, ease of control, and low capital costs. The disadvantages are generally higher heat flux density and burn out potential due to no natural limit of maximum heat transfer surface temperature. Electric heaters are 100% efficient in that all energy supplied to the heater is released to the tank as heat.

Material Handling and Degree of Automation and Controls

Due to the large part sizes, overhead hoist systems tend to be the most common method of transferring loads from stage to stage. These systems can range from simple manual hoists to fully-automated threeaxis systems where all movements are computer controlled and monitored.

If it is a low volume cleaning operation and advanced measures of process controls and documentation are not required, then a manual transfer system maybe sufficient. All transfers are timed and controlled via an operator. This basic system has the greatest operator objectivity and potential for operator error. However, the advantage is that the operator interfaces directly with the system and can visually inspect the parts between each process. If more process time is required and the recommended maximum process time has not been exceeded, the operator has the ability to increase the cycle time by putting the parts into the tank for additional cleaning.

When a higher degree of automation, process control and documentation are required and/or the anticipated cleaning volumes are high, fully automated transfer systems can meet these requirements. The more advanced systems utilize a control process commonly referred to as "dynamic scheduling." Dynamic scheduling features greatly enhance the process engineer's capability of performing complex recipe mixing with high production and/or high flexibility requirements. Hundreds of recipes can be intermixed. With databases of several thousand part numbers, the user can run any combination of racks or loads in any sequence and get consistent quality on every part, automatically. Simple to fill out menus for immersion times, drip times and desired min/max times can be employed.

With the proper software, detailed logs are automatically saved and customized reports can be generated. This greatly enhances the traceability of each part as it is processed though the cleaning system.

Ancillary Equipment & Waste Minimization One method to reduce waste treatment volumes is to extend the chemical bath's operating life. By removing suspended solids and floating contaminates, one can reduce the frequency of having to dump or waste treat thousands of gallons of chemical solutions. Suspended solids can be efficiently removed with basic cartridge or bag-type filtration. Recommended total tank turnover rates of 2-5 times per hour are common. With process tanks that see excessive soil loading (usually the first wash stages), higher LPM volumes are recommended.

Filtration in these types of applications commonly takes place at the macro particulate range of the filtration spectrum. Sand and grit fall into this range. The smaller the filtration media's micron rating, the greater the amount of soils which can be removed. Most filtration systems are designed with enough flexibility to enable the user to use a wide range of filtration media sizes. "Polishing" filtration systems operate in ranges as low as 50-100 micron (about the size of a human hair), while the systems designed for large soil loads may operate well above 1000 microns. When specifying the desired level of filtration, it is best to work closely with the equipment manufacturer and the chemical supplier. In addition, some engine manufacturer's standard procedures may have required levels of filtration for specific process stages.

If filtration of a higher level is required/desired, ultrafiltration can remove contaminates in the 0.001 to 0.1 micron size range⁹. These types of systems are designed to remove contaminates such as emulsified oils, rather than standard carbon dust and dirt. When considering this form of filtration, work very closely with the chemical supplier to ensure that their products are compatible.

Floating contaminates can be removed by incorporating a side stream coalescing system. On a continuous basis, solution on the top of the process tank is sparged to an overflow trough, which drains to the coalescing tank. This tank is designed in such a way as to create a "quiet zone" which provides ample time for the floating contaminates (some oils, carbon, dust, etc.) to pop from the solution, then be efficiently removed. The cleaned solution is then pumped back to the process tank. Its return flow is what creates the sparging effect across the top of the solution. When considering coalescing as an option, it is imperative that the cleaning chemical formula promotes the splitting/floating of oils and is not an emulsifying type of cleaner. Many OEM standard procedures will specify that the rinse water is treated for dissolved solids such as minerals and salts. Methods such as reverse osmosis and deionizing resin bed systems are quite common. However, deionized water is the most common form used in final rinse stages where high levels of rinse water purity are required¹⁰. These systems are usually leased from a local water treatment provider, who will maintain them as part of their service. Some local water supplies are so high in dissolved solids that treated water may not be optional, as their mineral content can have adverse effects on the final product.

Vender/Supplier Selection

After determining the basic requirements for the cleaning system, such as the number of process tanks, volume requirements and the preferred method of material handling, it is time to solicit potential suppliers for bids. Selecting the preferred company or companies to build the new cleaning line is a critical step in the process of designing and installing a new overhaul line.

Thorough Understanding of the Engine Overhauling Industry

Engine overhauling is an industry with very unique requirements for reasons detailed in this paper. The chosen vendor should have a thorough understanding of all of these aspects. Part size, part cost and unique cleaning chemicals require special attention and have specific requirements that the prospective equipment manufacturer should fully understand. Engine manufacturers will have minimum requirements and design requirements which some vendors may have never had exposure to, or experience in designing. What they may have previously built and is their standard design may not be appropriate in an engine overhaul line.

Industrial Cleaning Experience

There are many issues that separate the cleaning industry from other chemical processing applications such as plating or coating lines. Effective cleaning systems require industrial designed process tanks with dependable industrial mechanical agitation in the form of liquid agitation, part agitation or ultrasonics. Engine cleaning lines are no longer just large soak tanks. The supplier should have proven experience with one or more of these methods.

Customer References

References are a good way to not only find out about the company's product, but they also enable you to find out what type of after-sales support can be expected. As the engine overhaul business changes, it is critical that the supplier be positioned to address these changes. Contacting references can be one way to measure a vendor's after-sale support.

Obviously, a potential vendor will provide satisfied customers as references. So, it is probably a given that the references will speak highly of the supplier and the product. For this reason, it is important to inquire on other issues such as why this vendor was initially chosen over others, what is the percentage of operating uptime/downtime, what are the typical maintenance requirements and how user friendly is the system. It is also helpful to visit some of these references in person for obvious reasons.

Pricing

Traditionally, price has been a driving factor for cleaning acquisition projects. When considering costs, factor in more than the purchase price. Consider the cost of ownership, which will include, process efficiencies, usage costs (power requirements, chemical usage estimates, etc.) and cleaning yields. 100% first time cleaning versus the need to re-clean, represents a significant usage cost savings. In addition, factor in costs associated with warranties, extended warranties and guarantees.

When comparing pricing between two or more vendors, whenever possible, ensure that "apples are being compared to apples." Ask for as much detail as possible in the proposal so that an educated, objective comparison can be made. For example, one vendor may consider a sufficient liquid agitation rate to be 190 LPM (\approx 50 GPM), while another may have quoted 1150 LPM (\approx 300 GPM). If the process tank sizes are comparable, the differences between these rates in this example are significant and so are the costs associated with building them.

Summary and Conclusion

The aerospace engine overhaul industry is a dynamic industry which is constantly changing as aircraft and components change. Current trends include:

1) Increased process tank sizes due to larger engines and components. 2) The updating of soak tanks with the implementation of mechanical agitation to improve cleaning and reduce cleaning cycle times. 3) The reduction and elimination of solvents due to new environmental regulations. 4) Increased process control and higher levels of traceability to meet today's higher standards. 5) A move towards cellular cleaning to minimize in-process material handling costs and to bring total control of the part back to the work cell.

The engine overhaul industry is unique in many ways. Part sizes and variances, exotic metals, high component costs and requirements for high levels of traceability are just a few. Even with these unique issues, the basic cleaning formula still holds true. When designing a new cleaning line or improving an existing line, it is important to understand this basic cleaning formula of time, temperature, chemicals/concentration and method of cleaning. Each variable has a direct effect on the others. By changing one factor of the formula, it may have an exponential effect on others.

When designing a new cleaning line, one must determine: 1) The optimal number of process tanks. 2) The proper tank size and dimensions to accommodate the parts in the best orientation for the most effective cleaning. 3) The method of agitation that is most effective in your specific application at removing the soils. 4) Determine which method of heating best fits the application/situation and how to properly size the heating capacities of the process tanks to ensure that the recommended operating temperatures throughout the processes are maintained. 5) Determine what level of automation and material handling is needed to meet the volume requirements and provide the desired level of operator interface. 6) Which ancillary equipment may be advantageous to minimize the system's waste stream generation.

One of the most critical decisions in designing a cleaning line is the selection of a vendor. When considering vendors one should include the following

in the decision making process: 1) Do they have a thorough understanding of the engine overhaul industry and those requirements that make it unique? 2) Do they have industrial cleaning experience and have experience designing systems with mechanical agitation? 3) Do they have strong references and experience cleaning and handling similarly sized parts, if not direct experience with cleaning in the aerospace industry? 4) When comparing system costs, consider the usage cost, not just the initial purchase cost. 5) Request detailed proposals so an educated, objective decision can be made.

Projects of this size, complexity and magnitude require a great deal of research, time and effort. By thinking it through and using a step-by-step approach in the decision making process, it can simplify the complexity of the project and help to guarantee that the best system for your specific application is selected.

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Coatings Applied by High Enthalpy Plasma Spraying with Axial Feed

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A novel plasma spraying technology is described. By feeding the powder axially into a high enthalpy plasma plume, significantly higher spray rates and deposit efficiency are achieved, leading to improved economics of the spray process. Hard chrome replacement, wear resistant, corrosion resistant as well as thermal barrier coatings deposited by axial feed plasma are presented and discussed.

Although plasma spray equipment has been used to deposit coatings for many years now, plasma gun design has remained relatively unchanged. One of the greatest shortcomings of conventional plasma is the arc instability leading to difficulties to control coating quality and resulting in low deposit efficiency, i.e. for every pound of powder fed into the gun, only a small portion ends up as coating on the part. Traditional plasma guns spray many materials with low spray rates at deposit efficiency sometimes considerably less than 50%. Many of the low deposit efficiency materials are also sometimes the most expensive. Since the materials represent the largest single factor in the total cost for any plasma coating, low deposit efficiency is a serious process deficiency.

For many of the past years, plasma spray technology was driven by aerospace applications, primarily for jet engine components, and process cost was secondary to coating performance. Since then, competition has forced even the aircraft engine manufacturers to become extremely cost conscientious. More importantly, the use of plasma spray coatings is now much more widespread and new applications are often limited only by cost. Productivity and cost are very important issues for all manufacturing operations, so improvement of plasma spray efficiency is now a critical need. Strict procedures quality control require regular laboratory testing to confirm equipment performance. This can add to the cost as well as reduce overall productivity. Therefore, improved plasma spray process stability and reproducibility are today's stringent needs.

The High Enthalpy plasma technology offers a high degree of process stability and improved coatings reproducibility, combined with high spray rates and high deposit efficiency. These features create the conditions for an increase in productivity of up to three to five times and a reduction of coating cost with as much as 50%. In addition, superior quality coatings can be easily applied industrially and novel coatings can be researched and developed in the laboratory. Four major conceptual features characterize traditional plasma technology:

- 1. The electric arc root is not stabilized, i.e. the anodic root fluctuates axially and also works in arc re-strike mode [1]
- 2. The anode electrode is the same with the barrel of the gun
- 3. The operating arc voltage is relatively low and usually drops in time with electrode wear [3], [4].
- 4. The powder injection takes place relatively close to the arc root resulting in a turbulent and often-unpredictable interactions between the powder feed flow and the arc.

These features concur to reduce the overall efficiency of the spray process.

It is known that the anode attachment of the electric arc root is a highly turbulent phenomenon when hundreds of amps discharge into a "hot spot" localized on the surface of the anode. Since the anode is also the gun barrel, the injection of the powder takes place in the proximity of the arc root attachment, often resulting in an interference between the plasma turbulence created by the arc root and the powder flow.

The random movement of the arc root due to axial fluctuations and the arc re-strike combine to affect negatively the stability and uniformity of the spray process and the resulting coating properties [2]. Arc re-strike itself is a highly detrimental phenomenon. The re-strike of the arc root creates repetitive moments of virtual plume shrinkage [1] with adverse effects on particle melting, trajectory and velocity.

More recently, there have been attempts to correct some features of the traditional plasma technology. However, these have resulted in somehow complicated designs with as many as three sets of cathode electrodes being operated simultaneously inside the plasma gun [5], [6], [7].

The High Enthalpy plasma technology (Fig.1) resolves the shortcomings of the traditional plasma by acting in several important ways:

- 1. The electric arc root is stabilized and the arc re-strike is practically eliminated [8].
- 2. The anode is separated from the gun nozzle (barrel) [8].
- 3. The gun operates at significantly higher voltages [8].
- 4. The powder feed flow is optimized for different spray applications by injection either radially [9] or axially [10] as well as simultaneously whenever desired.
- 5. Only one cathode electrode is used in the plasma gun [8]

By using a proven and patented plasmatron design [8], the arc is elongated and its root is stabilized into the bore of a long life anode electrode (Fig. 1). The anode electrode also provides for a diffusion of the arc root without generating stationary surface "hot spots" The gun nozzle (barrel) and the powder injection port are separated from the anode electrode [8], [9], [10].

This new plasma technology concept achieves the following:

- 1. By stabilizing the arc root and by eliminating the arc re-strike, a constant voltage arc and a stationary and uniform plasma are generated. By diffusing the arc root and by working with higher voltage-lower amperage arcs, the electrodes wear is reduced and the long-term process stability is highly improved. By separating the anode from the gun nozzle and the powder injection, the turbulent interaction between the arc root phenomena and the powder feed flow are practically eliminated. This results in increased powder entrainment and less air entrapment in the plume.
- 2. By stabilizing the arc length and the axial fluctuations of the arc root, a constant and stable voltage is generated. Typical arc voltages for High Enthalpy plasma are between 200-250V depending on the specific spray parameters. These higher voltages induce increased ionization and higher plasma enthalpy. By working with ternary plasma gas mixtures such as

Ar+N2+H2 (He), combined with the high arc voltages, an elongated plasma plume is generated having enhanced heat capacity and thermal conductivity. These features translate in substantially higher spray rates and deposit efficiency.

- 3. Powder injection is an important step in plasma spraying. High Enthalpy plasma can work in both powder injection modes i.e. axial and /or radial therefore maximizing the spray output for the entire range of powder materials.
- 4. By using only one gas cooled tungsten cathode the High Enthalpy plasma becomes uncomplicated and reliable.

Due to the use of a stabilized plasmatron technology, the high enthalpy plasma gun can be operated at flexible power levels of up to 100 kW, thus covering all foreseeable industrial needs.

The High Enthalpy plasma offers new opportunities for increased productivity, reduced coating costs and increased reliability. The increase in spray rates can reach a factor of three to five. The higher deposit efficiency means coating cost savings through less powder wastage. Due to better melting and higher gas velocity, the high enthalpy plasma produces coatings with superior properties, which can be deposited at high spray rates. Examples are: dense and hard carbides (Fig.2), very low porosity chromium oxide (Fig.3), advanced chromium replacement coatings (Fig.4), high integrity abradables (Fig.5), advanced TBC's (Fig.6) etc.

Conclusions

High enthalpy plasma represents an important step forward in thermal spray technology that offers many significant advantages such as:

• Increased deposit efficiency leading to substantial cost savings. Many coating materials show increases of 30-40%.

- Better heating, melting and protection of the powder particles in the plasma, leading to improved coating quality (lower porosity and less un-melted particle content). It also reduces the oxide content in metallic coatings.
- Higher spray rates whenever desired. Most materials can be sprayed at rates of at least double the normal rates with the accompanying increases in productivity.
- Permits nozzle designs that maximize plasma spray output and coating performance.
- Permits advanced coatings development such as: high production abradable coatings, advanced thermal barriers, dense metallic and carbide coatings, production of nanomaterials and nano-coatings, production of FGM's, mixed and multi-layer coatings, MMC's etc.

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Fig. 1: Principles of the High Enthalpy plasma technology



Fig. 2: Tungsten carbide coating



Fig. 3: Chromium oxide coating

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Fig. 4 Hard Chromium replacement coating



Fig. 5 Al-Si/ Polyester abradable coating



Fig. 6 Dense YSZ thermal barrier coating



Fig. 7 General view of the High Enthalpy plasma spray gun

Important New Tools for Plating & Anodizing Engineering

Roger Mouton and Mark Thede, Stewart Technologies, Inc., Tempe, AZ 85282

Electroplating and anodizing process energy and material costs are very important considerations in product manufacturing, but the most important criteria, however, are the overall quality and plated uniformity of deposited metals or anodized coatings. Sophisticated plating and anodizing simulation tools help to obtain significantly better results. New simulation tools are now available that will run on PC/Windows and can point the way to optimizing many common electrolytic processes. The tools are versatile and user-friendly and have been designed to optimize electroplating and anodizing cells and their associated rack configuration. Sophisticated and accurate analyses are required to determine electrode potentials, distribution of deposited thickness, and true current densities. Good simulation tools can assist engineering teams to simulate and design optimum rack configurations based on the geometrical description of the rack, the parts to be plated or anodized and from calculation of the electrochemical properties of the process being studied.

For more information, contact: Roger Mouton or Mark Thede Stewart Technologies, Inc. 730 West 22nd. St. Tempe, AZ 85282 480-966-8333 FAX: 480-966-8444 sales@platingsystems.com We can think of very few plating applications that are as critical or more important than Airline and Aerospace plating. Functionally, plated or anodized substrates in aerospace and airline service see some of the most rigorous work cycles and hostile environments of any parts manufactured in industry today. It's especially important that plating deposit uniformity and integrity are maintained in the plating process.

An example that comes to mind is hydrogen embrittlement induced by the plating process. It is generally believed that hydrogen embrittlement is simply inherent in some electroplating processes and that controlling the current density on the substrate can minimize its effect.

Hydrogen embrittlement from a plating process would usually be more severe on the high current density area of a plated substrate than on intermediate or low current density areas. Emerging electroplating technology software is capable of creating accurate 3D plating simulations that can give engineers an important tool in minimizing the highto-low current density differences on a plated substrate.

An example of the importance of plating deposit uniformity can be found in a production plating environment....a scenario where numerous parts are mounted on a plating rack. To achieve the required minimum thickness on the inner parts, over-plating of the outer parts occurs. Where there is overplating, or non-uniform plating, there is usually a large current density variance. Over-plating, or non-uniform plating, has a detrimental effect on the plating cycle time, not to mention the overall consumption of plated metal. Numerous examples abound.

Figure 1 is a photograph of a plating rack holding 216 pulleys. These pulleys are utilized in the manufacture of engine components, and are plated for function: they must have good balance because they spin at high revolutions, but they are also plated for corrosion resistance.

In order to achieve the specified plating thickness, serious over-plating occurred on the outer edges of the exterior rows of pulleys. This resulted in a high rate of scrapped parts, potentially constituting the entire outer rows of pulleys, or up to 38% of the total on both sides of the rack.



Figure 1

Analysis of the process utilizing 3D modeling in electroplating simulation, *Figure 2*, showed that individual pulleys were being over-plated around the perimeter edge by nearly 100%.



For a pulley that must be properly balanced in order to provide a smooth running engine component, this clearly is unacceptable. Accurate, 3D electroplating simulation permitted optimizing the entire process so that current density variations were minimized, overplating was reduced, and plating efficiencies were maximized.

In *Figure 3*, the color red represents the thickest deposits. The optimum, or specified thickness shows as a light blue color.



Figure 3

As this example was an existing plating operation, the ability to make major changes to equipment configurations was limited. The plating engineering effort therefore concentrated on optimizing the rack design.

Using 3D modeling, it was found that the addition of current thieves around the outer edges of the pulleys produced substantially better plating results so that virtually no parts were scrapped. A detailed section of the plating rack is depicted with initial, intermediate and final simulations, *Figure 4*.



Figure 4

The goal of the plating simulation steps in this case is to get the colors to be more uniform, thus signifying better plating deposit thickness distribution. This minimizes current density differences and enables the plating engineer to make informed decisions about plating most substrates.

The following examples represent additional simulations depicting several "what if" scenarios: in *Figure 5* alternate anode size and shape are simulated.



Figure 5

In *Figure 6*, a graphically detailed current density analysis of both the electroplated part and the anode is visible. Take special note of the "hot spot" on the anode.

An integral component of the technology makes it possible for engineering CAD drawings to be imported in a number of formats. They are analyzed and then modeled so that the parts they represent will plate in accurate simulations. This has been immensely helpful in the design and building of new plating equipment to accommodate specific and demanding plating specifications.



Figure 6

Plating deposit uniformity is especially important where precious metals are concerned. Overplating is costly. It's possible with accurate 3-dimensional modeling to "read" a specific location of the plated substrate and determine its thickness at any given point.

Further, the total amount of plated metal weight on the part can be calculated. With a "before and after" simulation of plating and optimization, it would be possible to calculate plated metal costs and better understand raw material requirements. This could be especially useful for determining the processing characteristics of new part designs. Such detailed analyses have not been possible with plating technologies historically available to industry.

Optimization of the plating process can apply to all electrolytic manufacturing disciplines where there is a defined electrolyte and a known cathode entity. Examples of other applications, i.e. plating valve components, *Figure 7*, demonstrate plating optimization.



Figure 7

Figure 8 describes a plating fixture simulation for hard chrome plating of these valve components made possible using 3D modeling.



Figure 8

Prior to the plating optimization on these valves, hard chrome overplating and then "grinding back" to proper tolerances had been costly, but necessary, to produce acceptable parts. This is an example of technology that radically altered the valve manufacturing cycle. Plating to optimal thickness tolerances vs. plating and subsequent mechanical metal removal is definitely preferred.

Engineering the plating or anodizing current to preferentially flow where it's needed is key to optimizing industrial electrolytic manufacturing processes, as we know them. However, coating thickness uniformity is not necessarily the primary concern or difficulty for anodizers. Current density uniformity is however, important.

When the anodize process is initialized, current density can get very high because the oxide film is very thin and the resistance is low. If the anodizer isn't careful, the current density will get too high, and might cause burning. Many anodize systems have a "ramp up" cycle, keeping the voltage low and increasing it slowly or in specific increments as the oxide film increases. At a certain point, when the film is of sufficient thickness (after the "ramp up" period), the voltage levels out and stays fairly constant. To be able to determine the optimal point and avoid the ruin or burning of parts has been a "trial and error" process.

After a certain amount of time in the anodize tank, the oxide film reaches a "saturation" point, where the thickness doesn't increase much - even with current still applied. Determining where this point might be could aid in decreasing dwell times and increasing production, i.e. only leaving parts in the anodize tank as long as needed. Typical current density ranges for commercial anodizing are 10-20 asf and sometimes as high as 30 asf. If the current density is higher, the oxide film forms quicker. but is harder and less porous. If it's too high you get burning. If the current density is too low, <10 asf for example, the film may be too thin, too soft, or too porous. Finding an ideal anodizing current density might be possible using simulation tools.

The simulation software is based upon mathematical models and a numerical method utilizing boundary element analysis, taking into consideration the overall configuration of the tank and utilizing the characteristics of the electrolyte itself in analyzing the process.

In *Figure 9*, the four basic elements of a plating tank are mapped with special consideration to the cathodic boundary Γ_{C} , anodic boundary Γ_{A} , plating tank Γ_{R} . The electrolyte Ω is effectively limited by each of these items.



The plating process (P1) can be described by finding the potential u(x) in the electrolytic domain, and the potential difference φ between the two electrodes:

$$\int -\nabla u(x) = 0 \qquad \text{in } \Omega \quad (1)$$

$$\sigma (\partial u / \partial n) = f(u(x)) \qquad \text{on } \Gamma_{\rm C} \quad (2)$$

P1
$$\langle -\sigma (\partial u/\partial n) = g(u(x) - \sigma)$$
 on Γ_A (3)

$$\sigma \left(\frac{\partial u}{\partial n} \right) = 0 \qquad \qquad \text{on } \Gamma_{\mathrm{R}} \quad (4)$$

$$I = - \int_{\Gamma_{\rm C}} \sigma(\partial u / \partial n) d\Gamma_{\rm C}$$
 (5)

The total current *I* generated by the rectifier corresponds to the dual quantity φ between the two electrodes. The functions *f* and *g* represent cathodic and anodic polarization laws, describing the potential gap at the electrode/solution interface. These electrochemical behavior laws (*f* and *g*) are non-linear. Thus the entire system (P1) is non-linear as well.

The problem is solved by boundary element analysis, coupled with a Newton-Raphson technique. At the power source, the dual global quantities (current *I* and potential difference φ) are linked by a non-linear function (a generalized Ohm's law).

The resolution of (P1) is inadequate, so an algorithm was developed, monitored by global current *I*. This current takes into consideration the working current density as recommended by the chemical manufacturer of a particular electrolyte additive. Calculated current densities are then utilized with Faraday's law to predict the plated deposit.

CONCLUSIONS:

The electrolytic system can be broken down into its many basic elements:

- Tank Design
- Cathode Design
- Anode Design
- Chemistry & Operating Parameters

These elements are better understood by accurately determining how each interacts with the others. Analyses of these complex interrelationships are made possible by new electrolytic process engineering technology rooted in software development, that is driving modern manufacturing to greater cost and cycle time efficiencies.

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Electrodialysis of Chromic Acid Anodizing Solutions for Bath Maintenance

An Environmental Technology Verification-Metal Finishing (ETV-MF) Pollution Prevention Center Test Report

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The ETV-MF Center conducts performance verifications of innovative, commercialready technologies designed to improve industry performance and achieve cost effective pollution prevention solutions. Test plans are developed cooperatively between Concurrent Technologies Corporation (CTC), the US Environmental Protection Agency (EPA) and the technology supplier. Verification is conducted under strict EPA quality guidelines in metal finishing shops under actual operating conditions.

This paper will present the verification test results of an electrodialysis technology for maintaining chromic acid anodizing solutions. The test methods, data analysis, and conclusions will be presented, including the environmental and economic benefits of this technology. The presentation will conclude with an update of the EPA ETV-MF Center program and the status of other verification test projects.

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VERIFICATION TEST DESCRIPTION

The electrodialysis unit was tested, under actual production conditions, on a chromic acid anodize bath solution, at an aerospace contract anodizer. Chromic acid anodizing is performed on various aluminum parts in one of two independent parts processing lines: a 27-foot or a 62-foot line. The verification test evaluated the ability of the electrodialysis unit to purify the chromic acid anodize bath solution of process contaminants in the 27-foot chromic anodizing line.

Testing was conducted during two distinct five-week test periods (Baseline and Operational Modes):

- During the first test period (Baseline Mode), the electrodialysis unit was turned off, and the chromic acid anodizing bath was monitored to determine the buildup rate of process contaminants. Aluminum parts were anodized at typical processing rates.
- During the second test period (Operational Mode), the electrodialysis unit was turned on, and the chromic acid anodizing bath was monitored to determine the rate of process contaminant removal. Again, aluminum parts were anodized at typical processing rates.

Historical operating and maintenance labor requirements, chemical usage, and waste generation data were collected to perform the cost analysis.

TECHNOLOGY DESCRIPTION

The electrodialysis system purifies and reconditions spent chromic acid by circulating it through a specialized electrochemical cell. Anodizing solution is recirculated between the anolyte section of the electrodialysis cell and the anodizing process tank. During this process, trivalent chromium in the anodizing solution is oxidized to hexavalent chromium, and metal cations are transported to the catholyte solution through a porous, polymeric membrane separating the anolyte and catholyte compartments of the cell. The treated process solution is then returned to the anodizing bath. The metal contaminants removed from the process solution are kept in solution in the catholyte side of the cell until the solution becomes saturated with contaminants. At the test site, saturated catholyte waste (100 gallons) from the electrodialysis unit is disposed of about four times a year.

VERIFICATION OF PERFORMANCE

In the Baseline Mode, six weekly grab samples were collected over a five-week period from the anodizing tank and analyzed to determine the buildup rate of process contaminants. In addition, weekly grab samples from the rinse tanks upstream and downstream of the anodizing tank were collected and analyzed for mass balance purposes related to the anodizing tank.

In the Operational Mode, five weekly grab samples were collected over a six-week period from the anolyte and catholyte sections of the electrodialysis unit in addition to the samples collected during the Baseline Mode. All samples were analyzed for process contaminants in order to perform a mass balance and determine the removal efficiencies of process contaminants from the anodized bath solution.

Eleven weeks after the electrodialysis unit was turned on, samples were again collected. These samples are designated as "1Q" in **Table 1**, and represent the chemical characteristics of the anolyte and catholyte at the end of the first quarter of the catholyte operating cycle, 11 weeks after the system was turned on.

Average analytical results for key parameters are shown in **Table 1.** Hexavalent chromium is the primary active ion in the chromic anodizing process. Trivalent chromium is the natural occurring reduced state of hexavalent chromium. The reduction from hexavalent chromium to trivalent chromium occurs in the anodizing bath over a period of time, and can be accelerated by temperature and pH changes, and chemical and electrochemical reactions. Aluminum and magnesium are the primary anodizing bath contaminants. A small amount of aluminum (0.39 g/l) is required for the aluminum anodizing process to occur. After six weeks of operation, the purified chromic acid anodized solution maintained a relatively steady chemical and contaminant composition similar to the anodizing solution at the time of electrodialysis unit start-up. The buildup of process contaminants in the anodizing solution was slowed, while the contaminant level in the catholyte increased dramatically, showing a contamination transfer across the polymeric membrane.

	Hexavalent	Trivalent	Total	Total	Total
	Chromium	Chromium	Chromium	Aluminum	Magnesium
	(by titration)	(by titration)	(by ICP-AES)	(by ICP-AES)	(by ICP-AES)
	g/l	g/l	g/l	g/l	g/l
Sampling week	Anolyte / Catholyte	Anolyte / Catholyte	Anolyte / Catholyte	Anolyte / Catholyte	Anolyte / Catholyte
0 - Baseline	48.0 / NA	< 1.1 / NA	49.0 / NA	3.6 / NA	0.27 / NA
1 - Baseline	48.0 / NA	< 1.1 / NA	46.0 / NA	3.7 / NA	0.31 / NA
2 - Baseline	48.1 / NA	< 1.1 / NA	42.0 / NA	3.8 / NA	0.25 / NA
3 - Baseline	47.5 / NA	< 1.1 / NA	43.0 / NA	4.0 / NA	0.26 / NA
4 - Baseline	50.5 / NA	< 1.1 / NA	50.0 / NA	4.5 / NA	0.32 / NA
5 - Baseline	51.5 / 20.6	< 1.1 / < 1.1	46.0 / 18.0	4.5 / 0.1	0.32 / 0.09
6 - Operational	52.6/21.3	< 1.1 / < 1.1	44.0 / 20.0	4.1 / 2.0	0.29 / 0.12
7 - Operational	52.9 / 22.5	< 1.1 / < 1.1	44.0 / 21.0	4.1 / 3.2	0.22 / 0.15
8 - Operational	53.5 / 36.1	< 1.1 / < 1.1	48.0 / 34.0	4.6 / 3.8	0.24 / 0.20
9 - Operational	53.8/41.5	< 1.1 / 1.7	46.0 / 42.0	4.4 / 5.4	0.21 / 0.25
10 - Operational	Thanksgiving holiday – no samples collected this week				
11 - Operational	52.7 / 51.6	< 1.1 / < 1.1	50.0/48.0	4.9 / 6.4	0.24 / 0.28
16 - 1Q	N/A	N/A	52.5 / 50.5	5.4 / 7.5	0.26 / 0.31

Titration = Standard sodium thiosulfate titration, <u>1999 Metal Finishing Guidebook</u>, Vol. 97, No. 1, Control, Analysis, and Testing Section – Chemical Analysis of Plating Solutions, Charles Rosenstein and Stanley Hirsch, Table VIII – Test Methods for Electroplating Solutions, page 538.

ICP-AES = Inductively Coupled Plasma-Atomic Emission Spectrometry (EPA SW-846 Method 6010B)

Table 1. Summary of Key Analytical Data

Oxidation of Trivalent Chromium to Hexavalent Chromium. The oxidation of trivalent chromium to hexavalent chromium in the anolyte and the transfer of hexavalent chromium across the polymeric membrane from the catholyte to the anolyte by the electrodialysis unit is marketed as one of the beneficial conversions performed by the electrochemical process. However, as can be seen in **Table 1**, trivalent chromium levels

were never above background levels in the anolyte; therefore, there was no quantifiable oxidation to hexavalent chromium. A slight increase in hexavalent chromium levels in the anolyte was observed, but since the test site adds chromic acid to the anodizing bath on a regular basis, this increase in hexavalent chromium concentration cannot be definitively attributed to the electrodialysis unit's electrolytic reaction. Hexavalent chromium levels measured by titration that are higher than total chromium levels measured by ICP-AES are due to uncertainties inherent in the precision of these two different analytical methods.

Contaminant Removal. Removal of the primary contaminants of the chromic acid anodize bath solution, aluminum and magnesium, are shown in **Table 2**. For the Baseline Mode, the average aluminum increase in the anolyte was 0.180 g/l per week. The average magnesium increase in the anolyte was 0.010 g/l per week. During the Operational Mode, aluminum and magnesium levels in the anolyte remained relatively stable, while the catholyte showed an average weekly increase of 1.053 g/l of aluminum, for an overall removal of 9,442 grams of aluminum (catholyte + clarifier overflow) from the anolyte solution over the six-week test period. Magnesium contamination was less pronounced, showing an average weekly increase of 0.0317 g/l for an overall removal of 355 grams of magnesium (catholyte + clarifier overflow) from the anolyte solution over the six-week test period. The electrodialysis unit proved to be an adequate technology for removing aluminum contamination from the chromic acid anodize solution at the test site; however, the unit was not able to completely arrest the contamination rise in the anodizing bath. Since the six-cell model tested is the smallest electrodialysis unit available, it is possible that a larger unit may solve this problem. However, since the electrodialysis unit was turned on when the anodizing bath was within 1.6 g/l of its upper limit for aluminum, the purification system was unable to prevent the anodizing bath from reaching the upper contamination limit, triggering disposal of the anodizing bath. It can be concluded that the electrodialysis system extended the anodizing bath life by slowing the contamination build-up rate, but due to the relatively short verification test period, the length of this extension could not be determined.

Anolyte		Start (g/l)	End (g/l)	Change (g/l)	Average Weekly Increase (g/l)
Aluminum	Baseline Mode	3.6	4.5	+0.9	+0.180
	Operational Mode	4.5	4.9	+0.4	+0.067
Magnesium	Baseline Mode	0.27	0.32	+0.05	+0.010
	Operational Mode	0.32	0.24	-0.08	-0.0133
Catholyte					
Aluminum	Operational Mode	0.085	6.40	+6.32	+1.053
Magnesium	Operational Mode	0.087	0.28	+0.19	+0.0317

Table 2. Contaminant Removal

Energy Use. Energy requirements for operating the electrodialysis unit at the test site include electricity for the analyte and catholyte pumps and the system rectifier. Electricity use was determined to be 6,366 kWh/day, based on continuous operation of the system.

Waste Generation. A waste generation analysis was performed using operational data collected during the verification test period, and historical records from the test site.

Waste generation data normalized to the amount of work processed over the verification test period showed an anodizing bath waste generation reduction of about 54 percent when the electrodialysis system was in use. Implementation of the electrodialysis system extended the life of the anodizing bath, thus generating less chromic acid waste. However, some of this waste reduction is offset by chromic acid waste generated by the system. The net reduction of concentrated waste generated from the chromic acid anodizing process when the purification system was in use is thus reduced to 46 percent.

Operations and Maintenance Labor. Operations and maintenance (O&M) labor requirements for the electrodialysis system were monitored during testing. The O&M labor requirements for the equipment were observed to be 2.8 hrs/wk. Accounting for savings in reduced labor associated with anodizing bath chemical additions, the system averages about 135 labor hours per year. O&M tasks performed during the verification test included daily inspections of the unit, recording of system parameters, and additions of chromic acid flakes to the clarifier to maintain the catholyte pH below 2.

Cost Analysis. A cost analysis of the electrodialysis system was performed using current operating costs and historical records from the test site. The installed capital cost (1993) of the unit was \$35,230 (includes \$33,630 for the system, and \$1,600 for installation costs). The annual cost savings associated with the unit is \$5,140. The projected payback period is 6.8 years.

SUMMARY

The test results show that the electrodialysis system does provide an environmental benefit by extending the bath life of the chromic acid anodize solution, thereby reducing the amount of liquid wastes produced by the anodizing operation without removing the required anodizing constituents of the bath. The economic benefit associated with this technology is primarily in reduced waste disposal costs associated with the life extension of the anodizing bath. Unfortunately, when the labor and electrical costs associated with operating the electrodialysis system are factored in, the payback period is approximately 6.8 years. As with any technology selection, the end user must select appropriate bath maintenance equipment and chemistry for a process that can meet their associated environmental restrictions, productivity, and anodizing requirements.

Using Aqueous Chemistry to Clean Aircraft Engine Tubing

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This paper chronicles the development of an aqueous cleaner that removes carbon, coke and fuel varnish from engine tubing, and will also describe the testing process to get its approval by the engine manufacturer and this presentation will describe the problem of removing carbon, coke and fuel varnish buildup in engine tubing caused by elevated temperatures, and describe the development of a cleaning chemistry that will remove the contaminants without damaging the tubing. The procedure for the cleaning process will be described.

For more information contact: Parky May Bergdahl Associates, Inc. 2990 Sutro Street Reno, NV 89512 775-323-7542 parky@bergdahl.com Introduction of a "new and improved" cleaning technique involves two distinct steps. The first is the development of a high quality cleaner and/or technique for the application. This would seem to be the main part of the process, but a second step is equally important. This involves the testing and acceptance of the new cleaner and/or technique. This paper chronicles not only the development of an aqueous cleaner that removes carbon, coke and fuel varnish without damaging engine tubing, but also describes the testing process required to get its approval by the engine manufacturer.

Over the years turbine engines have become larger, have developed greater thrust, and as a result have gotten hotter. The more heat around the tubing the greater the problem with buildup of carbon, coke, and fuel varnishes inside the tubing. The result is an unacceptable restriction in flow, necessitating periodic cleaning of the tubing. Even as this cleaning has become more necessary, the deposits have become harder to remove and the cleaning process has become both more difficult and more likely to damage the tubing.

At the same time this problem with cleaning of accessory components was becoming more serious, in Belgium there was a scientist working on developing a better, safer cleaner. Two main forces drove his research. First, there was simply a need for cleaners that were more environmentally friendly. Second, once the Montreal Protocol on "Substances That Deplete the Ozone Layer" was established in 1987, the interest grew from a "want" to a "need" for more environmentally friendly cleaners.

The solution to finding a product that would meet these requirements was to get away from petroleum and chlorinated products and create a cleaner based on water. This was not a new concept. The Ebers Papyrus, a medical document from about 1500 B.C., describes combining animal and vegetable oils with alkaline salts to form a soap-like material. While being quite environmentally friendly, these cleaners unfortunately were not particularly effective then or now.

It was clear that for effective aqueous cleaning a high-pH liquid would be required. The trick would be to figure how to use the very effective cleaning capacity of such a liquid yet eliminate many of the negatives attributed to caustic cleaners – such as health and environmental hazards and metal loss.

Another enhancement would be if the cleaner was a splitter rather than an emulsifier. The cleaner would thus be able remove contaminants without creating the emulsified by-products of traditional cleaners. As an added plus, the contaminants removed would also remain essentially intact, and should thus be relatively easy to remove from the cleaning bath. The result of this research was an aqueous cleaner with a pH of about 12.5 and a NFPA^{*} hazard rating of zero for Health, Reactivity, and Flammability. The cleaner turned out to be very effective in breaking up the structure of petroleum base contaminants without attacking metals or other substrates.

The cleaner was thus developed, and what seemed to be the hardest task was accomplished. However, the next step was to introduce this product into the aircraft engine overhaul market. Unfortunately, this process is best described as "you can't get there from here". The Catch-22 is that a turbine engine overhaul facility will not generally use a cleaner unless it has been approved by the engine manufacturer, and conversely an engine manufacturer will not approve a cleaner unless it has been tested on engine parts by an engine overhaul facility.

How could this stalemate be broken? In trying to get the new cleaner accepted – or at least evaluated – our strategy was to start in the middle and work in both directions. First we would have to complete required testing standards to prove the product's performance since we knew an engine manufacturer would not even

^{*} National Fire Protection Association

look at a cleaning product until certain specific tests were done. Next we had to find a willing engine overhaul facility that had a unique cleaning problem and convince them to evaluate our product.

First we had the required tests performed. They are: SAE ARP 1755B Effect of cleaning agents on aircraft engine materials (Stock Loss Test Method)

ASTM F 519-97 Type 1A.1 Standard Test Method for mechanical Hydrogen Embrittlement Evaluation of Plating Process and Service Environments (Passive Chemicals)

ASTM F 945-98 Stress Corrosion of Titanium Alloys

We were confident that the product would meet these requirements, and indeed passing the required testing turned out to be the easy part. All it takes is money and time. It is, however, important to pick a testing company that is well known and respected in the industry.

Once the testing was complete and the cleaner had passed the next step was to find an engine overhaul facility that would work with us, and an engine manufacturer to evaluate the effectiveness of our cleaner on actual engine turbines. This is by no means an easy task. You must convince someone that your product is truly better than any of the products they are already using, and even then they have to be willing to take the time and effort to develop a procedure, assign personnel and finally do the testing.

In our case we chose to approach United Airlines (UAL) because we had been doing business with them for over 30 years – providing them sealants and dispensing equipment – and had an established credibility with them. We made significant arguments about the desirability of the product; it is biodegradable, presents no hazards to employees, offers no hazards to substrates, and has no odor. The fact that the agent is a splitter rather than an emulsifier means that contaminants such as oil will float to the top of the cleaning bath for easy removal, meaning that the bath is not loaded with the contamination and thus will last much longer than traditional cleaners. However, even with this set of persuasive advantages, it was difficult to convince anyone to give us an opportunity to demonstrate the cleaner on actual parts. The first demonstration came when we had an opportunity to clean a Flame Arrester Assembly from a GE CFM 56 engine. This flame arrester operates at 1350°F and becomes coated with coke and carbon from the exhaust gasses produced from the synthetic turbine oil vapors in the gearbox. The part cleaned easily without any damage to its metal structure. The second demonstration was successfully cleaning a Fan Blade Spacer off this same engine. This spacer is coated with five layers of molydisulfide and then baked. This part was also cleaned easily with no damage to the metal substrate and no degradation of the etched identification numbers, which remained easy to read. However, we were disappointed to learn that even though neither the Flame Arrester nor the Fan Blade Spacer had an approved chemical cleaning process at that time, there was still no interest in pursing further testing of our product to develop one for these parts.

Our next attempt to establish a testing and qualification process began with demonstrating the cleaning capability on engine tubing. A lubricant supply tube to the number 5 bearing was being removed from service because of restriction in the tube from coke and carbon buildup. The tube was examined with a borescope and it was almost completely blocked.

The supply tube was placed in an ultrasonic cleaner filled with our cleaner and cleaned for 15 minutes. After rinsing the tube, it was again examined with the bore scope and it was found that there was no residual coke or carbon remaining. Many UAL engineers at the demonstration felt that this cleaning process would solve existing problems and save money on parts that were currently being scrapped.

What is the current status? Now, one year later, a testing procedure has been established to evaluate the effectiveness of our cleaner on engine accessory parts. However, surprisingly none are the accessory parts included in our cleaning demonstrations of the Fan Blade Spacer, Flame Arrester, or supply tubing!

How does this testing and qualification process advance? At the time that the overhaul facility agrees to do the testing, the engine manufacturer will issue a six-month conditional letter based on the laboratory testing results. Alternatively, the testing at the engine overhaul facility could be done on their own engineering authority.

This testing procedure has three principle sections. The first test has nothing to do with the cleaner but rather it is to determine if ultrasonic energy has any negative effect on the part. The second test is to establish that there is no negative effect on the part from the cleaner, such as stock loss. The last test is to evaluate the effectiveness of the cleaner in removing the contaminants.

The testing procedures to be used in evaluating the new cleaner are as follows: Requirements for testing:

One new nozzle set (set includes: orifices, nozzles, restrictors, and visco jets.) Six sets of unserviceable nozzle parts Ultrasonic unit Chemical (our product) and (a competitor's new product) Access to a weighing scale Access to a 10X microscope Mechanical support for flow checking of parts

Testing stages:

Control Set (NEW PARTS)

 Weighed and recorded
 Crack check conducted and recorded
 Ultrasonic cleaning (12 hour) with water only completed and recorded
 Weighed after ultrasonic cleaning and recorded
 Crack check conducted and recorded
 Flow check conducted and recorded

 Note: Operating temperature for all ultrasonic operations is 49°C (120°F).

2) Control Set

Weighed and recorded Crack check conducted and recorded Flow check conducted and recorded Ultrasonic cleaning (I hour) (with each chemical) completed and recorded Weighed after ultrasonic cleaning and recorded Crack check conducted and recorded Flow check conducted and recorded

Note: Control Set must be included in all other tests in the succeeding stages.

- 3) Unserviceable Set 1 (referred to in test data sheet as Used Set) Weighed and recorded Crack check conducted and recorded Flow check conducted and recorded Ultrasonic cleaning (1 hour) (with each chemical) completed and recorded Weighed after ultrasonic cleaning and recorded Crack check conducted and recorded Flow check conducted and recorded Note: Unserviceable Set 1 must be included in all other tests in the succeeding stages.
- 4) Unserviceable Set 2/ Unserviceable Set 1/ Control Set Weighed and recorded Crack check conducted and recorded
 Flow check conducted and recorded
 Ultrasonic cleaning (1 hour) (with each chemical) completed and recorded
 Weighed after ultrasonic cleaning and recorded
 Crack check conducted and recorded
 Flow check conducted and recorded

Note: For the following test, do not include the Control Set or the Unserviceable Set 1.

- 5) Unserviceable Set 3
 - Flow check conducted and recorded,
 - a) Ultrasonic cleaning (I hour)
 - b) Flow check conducted and recorded (If flow check fails retry with another set) Note: If flow check is successful re-test using four more sets.
- 6) Unserviceable Set 4 / Unserviceable Set 1 / Control Set

Weighed and recorded Crack check conducted and recorded Flow check conducted and recorded Ultrasonic cleaning (with each chemical) completed and recorded Weighed after ultrasonic cleaning and recorded Crack check conducted and recorded Flow check conducted and recorded

- 7) Unserviceable Set 5 / Unserviceable Set 1 / Control Set Weighed and recorded Crack check conducted and recorded
 Flow check conducted and recorded
 Ultrasonic cleaning (1 hour) (with each chemical) completed and recorded
 Weighed after ultrasonic cleaning and recorded
 Crack check conducted and recorded
 Flow check conducted and recorded
- Unserviceable Set 6 / Unserviceable Set I / Control Set Weighed and recorded Crack check conducted and recorded

Flow check conducted and recorded Ultrasonic cleaning (l hour) (with each chemical) completed and recorded Weighed after ultrasonic cleaning and recorded Crack check conducted and recorded Flow check conducted and recorded

Evaluate data collected from testing.

The results of this test program will be reported in the conference presentation.

Summary/conclusions

Introduction of a "new and improved" cleaning technique involves far more than the development of a high quality cleaner and/or technique for the application. An equally important and potentially much more difficult step is the testing and acceptance of the new cleaner and/or technique. This step must be successfully negotiated or even a superior cleaner and/or technique may never be adopted.

21st Century Process Surface Finishing Control at Pratt & Whitney

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The paper will provide an overview of Pratt & Whitney's new automated surface finishing facility in North Berwick, ME. The processes at this facility include surface treatment of nickel alloys and titanium, masking, demasking and nickel plating. The four process lines are fully automated. Concentrated process solutions are maintained with an automated bleed and feed system and centralized solution maintenance technologies, including diffusion dialysis. Water usage has been reduced and rinsewater quality has been improved through automated water treatment and countercurrent rinse systems.

Paper not available

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Corrosion protection of aluminum alloys by magnetron sputtering and ion implantation

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Corrosion protection of aluminum alloys for aerospace applications is mostly ensured by an environmentally hazardous chromate conversion treatment. As possible clean alternatives, we investigated magnetron sputtering of AlN_X coatings and ion implantation with passivating metals. The elemental composition of the treated surfaces was determined. Corrosion behavior was tested by carrying out potentiodynamic polarization scans. Sputtering and implantation possess a potential to promote the corrosion resistance of aluminum alloys.

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1 Introduction

Aluminum alloys are widely used in aerospace industry due to their low weight combined with relatively high strength. Among the most prominent of these alloys are AA 2024 and 6061 where precipitates are formed after quenching leading to a higher strength. But especially for copper containing alloy 2024 the precipitates like A½CuMg differ in electrochemical potential from the matrix and behave as local elements so that this alloy is more susceptible to corrosion. Careful surface treatments for corrosion protection have to be carried out consisting today mainly of a conversion treatment with chromate containing baths. But Cr^{6+} ions are known to be dangerous to health and environment so that cost intensive recycling procedures are enforced by law. Therefore, environmentally clean alternatives are highly desirable. Such processes are predominantly solvent based, galvanic treatments like phosphating with fluor and metals like Ti, Zr, Ce, Mn, and Ni¹⁻². Recent developments include protection with self-assembling organic molecules or silicon containing liquids³. But all of these processes are solvent based so that production and disposal of liquids may also turn out to be environmentally harmful.

For this reason we propose a gas phase deposition process for surface protection of aluminum alloys. This process produces no liquid waste and benefits from low material consumption so that there are no environmental concerns⁴⁻⁵. Ion implantation is a promising process because only the surfaces are treated at low temperatures preventing the bulk properties from being changed. As the implanted species are introduced into the material, there are no adherence problems as may be in the case of coatings. Implantation of transition metal ions into aluminum alloys has been shown to promote the corrosion resistance of aluminum alloys. There are reports on corrosion behavior enhancement by implanting ions of Mo⁶, Cr⁷, and W⁸, where Mo ion implantation is especially used for aerospace aluminum structures⁹. McCafferty showed that the implanted metals change the electrochemical state of the surface and alter the corrosion mechanisms¹⁰.

PVD coatings can be used to protect surfaces from corrosion attack^{5, 11-12}. A prominent example in aerospace industry is replacement of galvanic cadmium coatings by ion vapor deposited aluminum on steel fasteners¹³. Layers of sputtered AlN_X should provide a corrosion protection due to their chemical inertness. Aita and Tait found out that sputtered AlN_X layers can have a passivating effect on carbon steel¹⁴. McCafferty et al. observed a higher pitting potential in nitrogen containing aluminum surfaces¹⁵. Booske et al. showed that nitrogen containing surfaces of alloy 6061-T4 show a more noble pitting potential and very little corrosion attack in salt spray testing¹⁶.

On the basis of these results, we want to show that corrosion protection of standard aluminum alloys 2024 and 6061 is possible by coating with AlN_X and implantation with transition metal ions.

2 Experiment

Samples of AA 2024-T3 and 6061-T4 were ground with grade 600 und 1000 sand paper and cleaned with water and ethanol in an ultrasonic bath before processing. AlN_X coatings were deposited in a Leybold Z700 magnetron sputtering device. After pumping down to a base pressure of 10^{-4} Pa the process consisted of 10 min plasma etching of target and substrates followed by 10 min coating deposition. Sample temperature was approx. 190°C implying only little growth of precipitates which can even enhance strength of the material. The structure of the coatings was visualized by scanning electron microscopy (SEM) of cross sections.

Ion implantation was carried out in a Danfysik 1090 unit at approx. 150°C achieved by sample cooling. Ti⁺ and Cr⁺ ions were extracted from a sputter ion source and accelerated to 160 keV. The applied dose was 1×10^{17} ions cm⁻² for both species. Depth profiles of the chemical composition of the treated surfaces were obtained by glow discharge optical emission spectroscopy (GDOES).

The corrosion properties of the modified surfaces were investigated with potentiodynamic polarization scans (anodic polarization curves). The electrolyte consisted of 3% NaCl aerated deionized water and the potential was measured against a saturated calomel electrode (SCE). The measurements were carried out by an Ibendorf ECMC device. In this method the sample is not immersed into the electrolyte, instead the electrolyte contacts the probe just in an area of approx. 2 mm². Before scanning the voltage was kept constant at -1 V for 10 s. The voltage scanning speed was 0.2 Vmin⁻¹. The scans were repeated two times at different sites for statistical purposes. The corrosive attack was checked by salt spray testing according to ASTM B117. Testing was chosen to be 12 h until some change in surface appearance occured. The exposed surfaces were investigated afterwards by scanning electron microscopy.

3 Results

Magnetron sputtering of AlN_X coatings and implantation with Ti^+ and Cr^+ ions were applied to samples of 2024-T3 and 6061-T4. Table 1 gives an overview of the applied treatments.

Table 1 Summary of the applied tro	eatments.		
Aluminum alloy	Magnetron sputtering of AlN _X (fraction x)	implantation of Ti ⁺ 160 keV, 1 ⁻ 10 ¹⁷ cm ⁻² (max. concentration, at.%)	implantation of Cr ⁺ 160 keV, 1 ⁻ 10 ¹⁷ cm ⁻² (max. concentration, at.%)
2024-T3	0.25, 0.67	10	10
6061-T4	0.25, 0.67	10	10

 AIN_X coatings were deposited with two different nitrogen contents by adjusting the nitrogen flow during the sputtering process. GDOES analyses of the coated samples yielded values of x = 0.25 and

0.67 which correspond to nitrogen contents of 20 and 40 at.%, respectively. Coating thicknesses was estimated from SEM images to be approx. $1 \mu m$.

As a second treatment, Ti^+ and Cr^+ ions with a dose of $1 \times 10^{17} \text{ cm}^{-2}$ were implanted in samples of alloys 2024 and 6061. The elemental composition of these treated surfaces was quantified by high resolution GDOES and showed a gaussian like distribution of the implanted species with a maximum at a depth of 0.2 µm. Maximum concentrations of approx. 10 at.% were determined.

The altered electrochemical behavior of the treated surfaces was checked with potentiodynamic polarization scans. Fig.1 shows the polarization curves of the AlN_X coated samples, together with a reference scan of the uncoated surface (sample back). For AlN_{0.25} coated alloy 2024 (fig.1a) the pitting potential of $U_P = -0.75$ V_{SCE} is not shifted but the current increase for $U > U_P$ is somewhat less pronounced. For the coating with higher nitrogen content (AlN_{0.67}) U_P is shifted to -0.5 V_{SCE} and the anodic current rises more slowly. In the case of coated alloy 6061 a similar tendency can be observed in fig.1b. As this alloy is electrochemically less noble pitting occurs at a lower voltage of -0.9 V_{SCE}. The AlN_{0.25} coating already leads to a clear shift of the corrosion potential to -0.5 V_{SCE}. The increase of the corrosion current is less steep and noisy indicating that some passivation occurs. For the AlN_{0.67} coated alloy 6061 an even more shifted pitting potential (-0.27 V_{SCE}) is measured coupled with a very slow current increase.



Fig.1 - Potentiodynamic polarization scans of AlN_X coated alloys 2024 and 6061.

In fig.2 the polarization curves of Ti^+ and Cr^+ implanted alloys 2024 and 6061 are shown. For 2024 alloy (fig.2a) both implantations lead to a shift in pitting potential from -0.75 V_{SCE} to about -0.6 V_{SCE}. Ion implantation into alloy 6061 yields an even more pronounced shift from U_P = -0.9 V_{SCE} to -0.6

 V_{SCE} (fig.2b) The current rise is not straight upward indicating again some passivation during the pitting process.



Fig. 2 - Potentiodynamic polarization scans of Ti^+ and Cr^+ implanted alloys 2024 and 6061.

The protective effect of the applied methods as revealed in salt spray testing is shown in fig.3 with some examples for alloy 2024. SEM images were taken of the uncoated reference surface (fig.3a), AlN_{0.67} coated surface (fig.3b), and Ti⁺ implanted surface (fig.3c). As is obvious from fig.3a the unprotected sample shows a pitted surface whereas this is not the case for the coated and implanted sample. Cr^+ implanted alloy 2024 which is not shown here reveals some pitted areas. The AlN_{0.25} coated alloy 2024 exhibits only very few pits. For alloy 6061 there was no pitting detectable for any applied treatment.



Fig.3 - SEM images of alloy 2024 surface with different treatments after salt spray testing: untreated surface (a), $AlN_{0.67}$ coated (b), Ti^+ implanted (c).

4 Discussion

From the polarization curves it can be concluded that magnetron sputter coating with AlN_X (fig.1) and ion implantation with titanium and chromium (fig.2) lead to a higher pitting potential of the two aluminum alloys investigated. It also turns out that sputter coating of AlN_X layers with high nitrogen contents provides a more effective protection than implantation. AlN is a ceramic material so that AlN_X coatings with sufficient nitrogen content should be chemically stable. Due to dominant covalent bonding nitrogen rich AlN_X coatings are electrically insulating so that they are not able to form an electrode which would promote the corrosion process. The $AlN_{0.25}$ coatings are less effective in protecting the underlying material especially for alloy 2024 (fig.1a). This may be due to the stronger metallic bonding in this coating which favors corrosion. Additionally, SEM cross section images reveal that $AlN_{0.25}$ coatings show a more columnar structure (fig.4a) whereas the nearly stoichiometric $AlN_{0.67}$ layers exhibit no preferred orientation or grain boundaries (fig.4b). Thus migration of CI ions to the substrate is easier through $AlN_{0.25}$ coatings. In contrast, $AlN_{0.67}$ layers provide a very effective barrier for migrating ions suppressing corrosion reactions at the coating/substrate interface.



Fig.4 - SEM cross section images of $AlN_{0.25}$ (a) and $AlN_{0.67}$ coating structure (b).

As Aita and Tait showed AlN_X coatings are able to form Al(OH)₃ in aqueous solutions providing some passivation mechanism¹⁴. McCafferty and co-workers found NH₃ and NO_X on corroded AlN_X surfaces and also concluded an inhibition and repassivation mechanism¹⁵. This could explain the unsteady increase of the corrosion current in fig.1. As is obvious from fig.1 the copper containing 2024 alloy is more difficult to protect than alloy 6061 presumably due to the strong local elements (precipitates).

As can be seen in fig.2 implantation with Ti⁺ and Cr⁺ ions leads to a shift in pitting potential to the more noble direction but there is no significant difference between the two implanted species. The shift can be explained by the fact that titanium and especially chromium are passivating metals with a higher electrochemical potential than aluminum. The potential shift is consistent with the results of other groups who studied transition metal implanted aluminum⁶⁻⁸. In all cases where transition metals of group IV to VII were introduced into the aluminum matrix a reduced tendency towards pitting in corrosive environments is observed. This was explained by McCafferty who showed that the

electrochemical behavior of implanted surfaces is modified leading to a change in reactivity with OH⁻ and CI ions¹⁰.

The potential shift is less pronounced for the copper rich alloy 2024 which may again be an effect of the copper containing precipitates. These local elements hinder passivation reactions so that the current increase is relatively constant for $U > U_P$ (fig.2a). Implantation into alloy 6061 leads to a more pronounced passivation (fig.2b). In this case silicon containing precipitates may even enhance the passivation reactions.

The SEM images of salt spray tested samples confirm the protective effect of the applied methods although the differences between coated samples do not become as obvious as with polarization measurements. Further investigations and longer test periods will be done in future works. In general, pitting of larger areas which occurs for the unprotected sample (fig.3a) is suppressed by both applied methods. Salt spray tests also confirm that alloy 6061 can be easier protected than alloy 2024.

Although polarization curves show the same pitting potentials for Ti^+ and Cr^+ doped 2024 samples (fig.2) the salt spray test shows that in case of Cr^+ implantation pitting occurs. This may be due to chromium rich precipitates which may have formed in the implanted zone. This result makes clear that electrochemical and long term testing are complementary procedures which are both necessary to evaluate the corrosion resistance of treated surfaces.

5 Conclusion

In the search for environmentally clean corrosion protection treatments, magnetron sputtering of AlN_x coatings and implantation with Ti^+ and Cr^+ ions were applied to the common aluminum alloys 2024-T3 and 6061-T4. The corrosion behavior was tested by potentiodynamic polarization and salt spray testing. The results show that higher pitting potentials can be achieved by both methods. Alloy 2024 is more difficult to protect due to copper precipitates disturbing passivation reactions. AlN_{0.67} layers provide a better protection than AlN_{0.25} coatings. Implanted titanium leads to a slightly better protection than chromium although pitting potential is equal. The applied treatments generally promote passivating processes on the treated surfaces so that a reduced corrosive attack in salt spray testing is achieved. Therefore, magnetron sputtering and implantation of suitable materials are able to provide a corrosion protection of aluminum alloys.

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