DEVELOPMENT OF A SEMI-AQUEOUS CLEANING AGENT FOR METAL CLEANING APPLICATIONS

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ABSTRACT

A new semi-aqueous cleaning agent has been developed for metal cleaning applications. It has zero ozone depletion potential, a high flash point, mild odor, low toxicity and a high degree of biodegradability. It is designed to be rinsed with water from the surfaces of cleaned parts and to separate rapidly from the rinse water into a second phase containing the dissolved soils. This simplifies recycling or disposal of the remaining water phase. This new cleaning agent is more effective than CFC-113 for removing heavy grease and high-melting wax and about equal in effectiveness to 1,1,1-trichloroethane. In addition, it is compatible with a wide range of plastics and elastomers.

INTRODUCTION

Cleaning is required in the metal-working industry to remove oils, greases, coolants, abrasive polishing compounds and particulates, such as metal fines and shop soils. CFC-based cleaning agents and chlorocarbon solvents, such as 1,1,1-trichloroethane, are commonly used in vapor degreasing equipment to remove these soils. With CFC regulation now in place, and the phaseout of CFCs and 1,1,1-trichloroethane planned, users are analyzing their cleaning alternatives, including: alcohol, hydrochlorofluorocarbon (HCFC), high flash point hydrocarbon, aqueous and semi-aqueous cleaners. In addition, some users are modifying manufacturing processes to reduce or eliminate the need for cleaning.

Ideal replacements for CFCs and chlorocarbons would be "drop in" solvents with properties similar to those used in existing vapor degreasers. Several alternatives have been identified as potential replacements, but their commercial availability is several years away.

Although designed to be used in vapor degreasers, the HCFCs currently available are not true "drop in" replacements. They are more volatile than existing solvents, have lower exposure limits than CFC-113 and require specially designed degreasers for their containment. Replacements other than HCFCs require different types of equipment and have other drawbacks. For example, alcohols clean well, but are flammable; high flash point hydrocarbons are slow drying; and aqueous cleaners are less effective for removing heavy oils and greases from tight clearances. In addition, aqueous cleaners pose special waste disposal problems unless the soils removed can be effectively separated from the waste water. The term "semi-aqueous" refers to a cleaning agent that includes a surfactant in its formulation to allow slow-drying residues to be rinsed from cleaned parts using water. The use of a two-step, or semi-aqueous, cleaning process offers the advantages of superior removal of difficult soils from tight clearances and minimum contamination of the rinse water. A semi-aqueous cleaning agent may be formulated to have a low surface tension, allowing penetration into narrow spaces, and a high solubility for contaminants. In addition, the oil-in-water emulsion formed during rinsing can be designed to separate into a solvent phase containing the bulk of the soils and a water phase amenable to purification by standard waste-treatment techniques.

Many of the semi-aqueous cleaners available today were designed for the removal of solder flux residues in the electronics industry. This paper describes the formulation of a new semi-aqueous cleaning agent designed specifically to remove the greases, metal-working fluids, buffing compounds and waxes encountered in metal-working operations.

DISCUSSION

DEVELOPMENT OF AXAREL[®] 52 CLEANING AGENT

The work reported here led to the recent introduction of Du Pont Axare™ 52 metalcleaning agent. To arrive at its formulation, a wide variety of mixtures were evaluated. In addition to cleaning performance, the properties desirable in a semi-aqueous cleaner include: specific solvency, fast emulsion separation, low toxicity, high flash point, rust inhibition and a high degree of biodegradability.

Selective Solvency

Hansen solubility parameters were used in designing the formulation for the new cleaning agent. Solubility envelopes were determined on a map of polar versus hydrogen bonding parameters for soils commonly encountered in metal cleaning, including: cutting oils, a drawing oil, metal-working coolants, grease, a rouge buffing compound and a wax. With the aid of a computer program, solvent mixtures that had predicted solubility parameters falling within the envelopes of these soils were selected.

These solvent mixtures were combined with many different surfactants and were used to prepare semi-aqueous cleaning agent candidates. Several formulations were rejected on the basis of insufficient mutual solubility. Those remaining were further screened using standardized cleaning tests for the removal of cutting oil and grease.

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Emulsion Separation

One of the advantages of a properly designed semi-aqueous cleaning agent is its ability to separate from the emulsion formed during rinsing. This separation must take place rapidly, so that a reasonably-sized decanter can be used.

The time required for a stagnant cleaning agent-in-water emulsion to separate into a solvent and a water layer was measured by recording the position of the interface between the two layers as the emulsion settled. Emulsions were prepared by adding 90 ml of distilled water, plus 10 ml of cleaning agent, to a 4-oz capacity bottle and immersing the bottle in a constant-temperature bath. After reaching thermal equilibrium, the bottle was withdrawn from the bath and shaken vigorously for 1 minute. The contents were immediately poured into a 100-ml graduated cylinder that was pre-heated in the constant-temperature bath. The cylinder was returned to the bath and the position of the interface recorded versus time.

Figures 1, 2 and 3 show the interface position in the cylinder versus settling time. They illustrate three important variables affecting settling rate -- surfactant, temperature and solvent. Figure 1 illustrates the effect of surfactant choice, while Figure 2 illustrates that higher temperatures result in faster settling with some surfactants. (Temperature can also have the opposite effect, depending on surfactant choice.) Figure 3 shows that the solvent mixture chosen also affects settling rate with a given surfactant at constant temperature. Formulation 3, which separates the fastest at elevated temperatures, is the final composition chosen for the new semi-aqueous cleaning agent.



Figure 1. Effect of Surfactant on Emulsion Separation. 10% cleaning agent in water, 140° F.



Figure 2. Effect of Temperature on Emulsion Separation. 10% cleaning agent in water.



Figure 3. Effect of Solvent Formulation on Emulsion Separation. 10% cleaning agent in water, 140° F.

Rust Inhibition

Another important consideration in formulating a semi-aqueous cleaning agent is to prevent flash rusting of mild steel. Oil and grease on a steel surface protect it from corrosion; a freshly cleaned surface that contacts water will rust rapidly. Therefore, the rinse step used with a semi-aqueous cleaning agent provides ideal conditions for flash rusting. One approach is to add a rust inhibitor to the rinse water. Another is to include a rust inhibitor in the semi-aqueous cleaner itself to prevent rusting of cleaned parts contacted by uninhibited water.

There are two types of rust inhibitors, oily and dry-film. Both leave a protective coating on the metal's surface. Oily inhibitors are effective in preventing rust, but undesirable on finished products or parts that will be coated, brazed or welded. The usual dry-film inhibitors are water soluble and are incompatible with semi-aqueous cleaning agent formulations.

Several specially formulated solvent-soluble rust inhibitors were screened for use in our semi-aqueous cleaning agent. These inhibitors function by polar bonding of a very thin, dry layer to the metal surface. However, in order to be solvent soluble, these compounds cannot be as polar as the water-soluble inhibitors and, as a result, do not bond as strongly to the metal surface.

The inhibitor chosen for the final formulation is very effective in protecting freshly cleaned steel surfaces during the initial emulsion rinse step and during subsequent ambienttemperature rinses. If inhibitor residues are undesirable on finished product, they may be removed with hot water.

COMPOSITION AND PHYSICAL PROPERTIES OF AXAREL[®] 52 CLEANING AGENT

The resulting semi-aqueous cleaning agent combines a hydrocarbon base with a surfactant and a rust inhibitor to yield selective solvency, fast emulsion separation, low toxicity, high flash point, mild odor and excellent biodegradability. Table I lists typical physical properties of Axare[™] 52. Properties important in vapor degreasing, such as boiling point and latent heat of vaporization, have no relevance to semi-aqueous cleaners and are not given.

High Flash Point

The flash point of Axarel[™] 52 is 210° F; therefore, it is classified as a Class IIIB combustible liquid by the National Fire Protection Association. Heating Axarel[™] 52 lowers its viscosity and surface tension, improving its cleaning performance. Additionally, heating softens or melts greases and waxes, accelerating their removal. The high flash point of Axarel[™] 52 allows these benefits to be realized, while maintaining Axarel[™] 52 safely below its flash point. A maximum use temperature of 180° F is recommended.

Table I. Typical Properties of Axa	ıreľ"	52
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Property	Axarel [™] 52
pH (5% solution in water)	5-6
Flash Point (Pensky-Martens Closed Cup)	210° F (99° C)
Vapor Pressure, at 77° F (25° C)	<0.1 mm Hg
Odor	Mild/Low
Aromatic Content	0.2%
Specific Gravity at 77° F (25° C)	0.83
Viscosity at 77° F (25° C)	2.9 cp
Surface Tension at 77° F (25° C)	27 dynes/cm

Biodegradability

Axare[™] 52 has been tested by electrolytic respirometry and found to be highly biodegradable. Rinse water containing Axare[™] 52 at anticipated concentrations is non-toxic and non-inhibitory to bacteria. As with all organic fluids, however, it should not comprise a major portion of the feed to a biological waste treatment plant.

METAL CLEANING EFFECTIVENESS OF Axarel[™] 52

Removing Light Oil

To determine the effectiveness in removing light drawing oil, assemblies were dipped for 15 seconds in "Cutzol" 711 cutting oil and drained for 15 seconds prior to cleaning. Each assembly was then suspended for 60 seconds in either CFC-113 at 118° F, 1,1,1trichloroethane at 165° F or Axarel[™] 52 at 122° F. The assemblies cleaned in Axarel[™] 52 were agitated by stirring and rinsed in water for 60 seconds at 122° F. The other solvents were agitated by their boiling action.

After air drying, cleaned assemblies were extracted in 75.0 ml of CFC-113 and the absorbance of the extract was measured at 232 nm. The ratio of the absorbance of the extract to that of the extract of an uncleaned assembly was used to calculate the percent oil removed (Table II).

Removal of light oil is relatively easy and the performance of Axarel[™] 52, CFC-113 and 1,1,1-trichloroethane was essentially the same. In our experience, more difficult soils are required to reveal differences in cleaning agent performance.

Cleaning Agent	Temperature, °F	Average Oil Removed, %	
Axarel [™] 52**	122	99.9	_ · ·
CFC-113†	118	99.5	
1,1,1-Trichloroethanet	165	99.6	

Table II. Cutting Oil Removal from a Metal Assembly*

*Test assemblies consisted of nuts and washers on a single bolt, dipped in cutting oil and cleaned for 1 minute. **Axare^M 52 was mildly agitated by stirring; after cleaning, samples were water rinsed for 1 minute at 122° F.

† Other solvents were refluxed at their boiling points.

Removing Heavy Grease

The ability to remove heavy grease was measured by determining the cleaning rate for a steel coupon coated on one side with 1/16 in. of Shell Alvania Grease No. 2. Coupons were suspended in mildly agitated Axarel[™] 52 for various times and rinsed for 2 minutes in water at 122° F. They were then dried to a constant weight in a vacuum oven at 265° F. These drying conditions were shown to produce a negligible change in the weight of pure grease.

Coupons were also suspended in refluxing CFC-113 and 1,1,1-trichloroethane. After each cleaning time increment, they were allowed to dry and the amount of grease remaining was determined by weighing.

Figure 4 shows the results of these tests in which Axarel[™] 52 removed grease significantly faster than CFC-113 and essentially as fast as 1,1,1-trichloroethane.



Figure 4. Removal of Heavy Grease by Cleaning with Axare 52, CFC-113 and 1,1,1-Trichloroethane. The Axare™ 52 was only mildly agitated by stirring; after cleaning, the samples were rinsed for 2 minutes in 122° F water. The other agents were tested at boil.

Removing Wax

To evaluate effectiveness in removing waxes, assemblies were dipped in molten Carnauba wax, allowed to cool and cleaned as described previously. Axare™ 52 heated to 167° F was also tested. Figure 5 shows that heating Axare™ 52 close to the 180° F melting point of the wax speeds up the cleaning process, resulting in performance similar to 1,1,1trichloroethane.



Figure 5. Removal of Carnauba Wax by Cleaning with Axarel[®] 52, CFC-113 and 1,1,1-Trichloroethane. The Axarel[®] 52 was only mildly agitated by stirring; after cleaning, the samples were rinsed for 2 minutes in 122° F water. The other agents were tested at boil.

Using an Emulsion

Studies have indicated that using an emulsion of Axare[™] 52 in water may be beneficial for removing some soils, such as buffing compounds and greases. However, our preliminary tests indicate that oils are best removed by using undiluted cleaning agent. Emulsions respond to ultrasonic agitation in the same way as aqueous solutions. The undiluted cleaning agent, which is a high-boiling organic liquid, does not cavitate as readily as low-boiling solvents or aqueous solutions. However, several equipment manufacturers have reported successful cavitation of pure Axare[™] 52 using properly designed equipment.

COMPATIBILITY WITH PLASTICS AND ELASTOMERS

Measurements have been made to test the compatibility of the new cleaning agent with common plastics and elastomers. Results of these studies are given in Tables III and IV. Axare™ 52 is compatible with many materials; in general, it is more aggressive than CFC-113 and less aggressive than chlorinated solvents, such as 1,1,1-trichloroethane. Since compatibility is affected by different plasticizers, compounding agents and manufacturing processes, critical components should be tested under actual conditions before use.

The following materials appeared satisfactory for the construction of elastomeric gaskets and seals used in semi-aqueous cleaning equipment: Teflon and Kynar fluorocarbon resins; Viton A, B, and GF fluoroelastomers; Thiokol FA and ST organic polysulfides; Adiprene polyurethane; Hytrel polyester elastomer; and Kalrez perfluoroelastomer. Buna N and neoprene are not compatible.

Material	Tradename	Axarel [™] 52	% Wt. Chg.	_
ABS	Kralastic	0	-0.2	
Acetal	Delrin [®]	0	-0.1	
Acrylic	Lucite®	Q	-0.2	
Cellulose	Ethoce	3	2**	
Ероху		0	0.3	
Fluorocarbons PTFE PVDF	Teflon [®] Kynar [®]	0 0	0 0	
lonomer	Surlyn®	3	6**	
Nylon	Zytef	0	-0.2	
Polyacrylate	Arylon®	0	-0.2	
Polycarbonate	Tuffak	0	-0.2	
Polyester PBT PET	Valox [®] Rynite [®]	0 0	0 0	
Polyetherimide	Ultem®	0	-0.3	
Polyethylene	Alathon®	0	0.7	
Polyimide	Kapton®	0	-0.3	
Polyphenylene Oxide	Nory	0	0	
Polyphenylene Sulfide	Ryton [®]	0	0	
Polypropylene		2	1**	
Polystyrene	Styrom	3	5**	
Polysulfone		0	-0.2	
Polyvinyl Chloride	PVC	0	-0.1	
Chlorinated Polyvinyl Chloride	CPVC	0	-0.1	

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Table III. Compatibility of Axarel[™] 52 with Plastics*

*1-day immersion at 122° F (50° C).

**Surface change noted.

Key: 0 = Compatible

1 = Probably compatible

2 = Probably incompatible

3 = Incompatible

Material	Axareľ 52 % Wt. Change	% Linear Swell
Adiprene [®] polyurethane	2	0
Alcryn [®] hydrocarbon thermoplastic elastomer	10	5
Buna N acrylonitrile-butadiene	70	20**
Buna S styrene-butadiene	15	6**
Butyl rubber	100	30 [†]
Hypaion [®] chlorosulfonated polyethylene	15	6
Hytrel [®] polyester elastomer	4	1.4 -
Kalrez [®] perfluoroelastomer	0	-0.9
Natural rubber	150	40**
Neoprene polychloroprene	30	9**
Nordel [®] EPDM rubber	30	10 [†]
Silicone polysiloxane	50	15
Thiokol [®] organic polysulfide FA ST	-0.1 1.3	0 0.3
Vamac [®] ethylene/acrylic elastomer	40	15
Viton [®] fluoroelastomer A B GF	0.6 0.4 0.3	0 0 0.9

Table IV. Compatibility of Axaref[™] 52 with Elastomers*

*1-week immersion at 122° F (50° C). **Gross loss of tensile strength. [†] Surface disintegrated.

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DESIGN AND OPERATION OF CLEANING EQUIPMENT

Agitation Methods and Ignitability

Although the new cleaning agent formulation has a high flash point, fine mists of the material in air can be ignited. Therefore, application methods that avoid misting, such as submerged liquid jets, mechanical agitation, work-piece movement and ultrasonics, should be used. If direct sprays are used, they should be performed in an inert environment or with the equipment otherwise protected from ignition conditions. Semi-aqueous cleaning agents should not be used in vapor degreasers or unmodified aqueous cleaning equipment.

Preliminary experiments have indicated that sprays of water emulsions containing no more than 30 weight percent Axare™ 52 cannot be ignited in air.

Operating Temperatures

Elevated temperatures have proved effective in removing greases and high-melting waxes when using Axarel[™] 52. A maximum use temperature of 180° F is recommended.

Ambient-temperature rinse water conserves energy and minimizes removal of rust inhibitor from cleaned surfaces. In some cases, however, hot water may be required for effective rinsing. If steel parts are given multiple hot-water rinses, it may be necessary to add a water-soluble rust inhibitor to the rinse water. In most cases, drying will be required, especially if a spot-free surface is desired.

Process Design

In its most basic configuration, a semi-aqueous cleaning system involves dissolving the soil in the solvent; rinsing the cleaning agent and dissolved soil from the cleaned surfaces; and drying the parts. An air knife may be used to minimize dragout of cleaning agent and dissolved soils to the rinse stages. If multiple rinses are used, the rinses may cascade one to the other from last to first. This basic system may be sufficient for many applications.

Figure 6 shows a more elaborate system designed to take full advantage of the properties of a semi-aqueous cleaning agent. In this configuration, a cleaning agent-in-water emulsion is allowed to form in the first rinse stage, now referred to as the emulsion stage. The emulsion stage overflows to a decanter that separates the cleaning agent and soils from the water. Dragout from the solvent stage, with subsequent replacement by fresh cleaning agent, is usually more than sufficient to keep the soil concentration in the solvent stage low enough for effective cleaning. If dragout is excessive, solvent can be recycled from the decanter to the solvent stage. The amount of solvent recycled determines the equilibrium concentration of soil in the solvent stage.

The rate of emulsion drawoff to the decanter controls the equilibrium concentration of cleaning agent in the emulsion. The water from the decanter is recycled to the emulsion stage. If water-soluble soils build up in the recycled water, a small stream may be purged to waste treatment. The liquid level in the emulsion stage is maintained by feeding either fresh water or water from the first cascade rinse. An air knife is used to blow emulsion from parts leaving the emulsion stage and to minimize dragout to the rinse stages.

Parts leaving the last rinse stage will usually require drying. Conventional methods may be used, such as compressed air blow off, circulating hot air or water displacement.

Du Pont is developing the processes shown in Figure 6 for recovery of solvent from soils and for treatment of rinse water with the goal of a completely closed-loop system.



Figure 6. The Semi-Aqueous Cleaning Process.

ADVANTAGES VERSUS AQUEOUS CLEANING AGENTS

The two main advantages of semi-aqueous cleaning over aqueous cleaning are better soil removal and reduced waste disposal costs. Aqueous cleaners are not as effective in removing heavy oils and greases. A semi-aqueous cleaning agent contains solvents that can dissolve these soils and penetrate tight spaces because of its low surface tension.

Semi-aqueous cleaners also offer significant ecological advantages over aqueous cleaners. The solvent phase will contain most of the soil and can be separated from the rinse emulsion. The water remaining can be recycled in a closed-loop system or, in some cases, sent directly to a sewage treatment plant. The cleaning agent phase and its dissolved soils can be incinerated to fuel other operations. It is expected that in most cases the spent cleaning agent will not be classified as a hazardous waste.

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SUMMARY AND CONCLUSIONS

- 1. A new semi-aqueous cleaning agent has been developed for metal-cleaning applications. Designated Axarel[™] 52, it combines a specially formulated solvent base with a surfactant and rust inhibitor.
- 2. Using water, Axarel[™] 52 and its dissolved soils can be rinsed from the surface of cleaned parts and then rapidly separated into a recoverable second phase. This greatly simplifies disposal or treatment of rinse water.
- 3. In addition to easily removing light oils, Axare™ 52 is more effective than CFC-113 for removing heavy grease and high-melting wax. It appears to be about as effective as 1,1,1-trichloroethane.
- 4. Axarel[™] 52 has zero ozone-depletion potential, high flash point, mild odor and low toxicity, and is highly biodegradable.
- 5. Axare[™] 52 is compatible with a wide range of plastics and elastomers.

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