New Cleaning Technology — Low pH, Recyclable, Heavy-duty Aqueous Cleaners

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Many new aqueous-based cleaning technologies are introduced into the marketplace each year, claiming to be environmentally safe, worker friendly and non-hazardous, with minimal disposal requirements. Most of these "new technologies" are actually traditional high pH (>11), silicated aqueous products that exhibit good cleaning but typically poor recyclable properties, especially when subjected to ultrafiltration systems for contaminant removal. This paper will discuss a new recyclable cleaning technology having both a low pH (<10) and containing no silicate-type ingredients. The product's performance will be compared to traditional high-pH-silicated products in both spray and immersion cleaning applications. Further comparisons will be made concerning ability to recycle through polymeric and ceramic membranes in an effort to help reduce effluent waste streams. Several field studies will also be reviewed to determine the feasibility of incorporating this new cleaning system into real-world applications. Conclusion demonstrates that a recyclable, heavy-duty aqueous cleaning technology with broad metal compatability can be obtained in a low pH, non-silicated product consisting of the proper selection of synergistic cleaning and corrosion inhibition agents with the right physical properties.

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Before discussing the properties of the new low pH, recyclable, heavy-duty, aqueous cleaning technology, a short review of conventional alkaline, aqueous cleaner properties would be useful for comparison. These products are typically highly built with caustics, silicates, phosphonates and other builders with a pH in the 12–13 range. Silicates, such as sodium metasilicate, usually provide corrosion protection for aluminum and carbon steel. Often these cleaners will contain low levels of nonionic-type surfactants primarily for quick wetting of metal substrates and low foam control. It is not uncommon for these types of products to attack sensitive metals. One example is the dezincification of brass.

There are advantages and disadvantages to using conventional alkaline, aqueous cleaners. Advantages include good cleaning performance on many industrials soils including heavy greases and baked-on carbon soils. They also provide good corrosion protection on most aluminum and steel alloys which is important for many automotive and aerospace industries.

However these conventional products have some disadvantages as well. They include Health, Safety and Environmental issues due to high pH levels. Also incompatibility with different types of equipment and manufacturing materials, often due to high pH levels, can be a concern. White, powdery residues often left behind by silicates are not only unsightly but may interfere with post treatments, such as coatings or painting.

As a result of these disadvantages, a project was initiated to develop a lower pH, aqueous based product with the same cleaning profile as a higher pH analog. The specific target properties for this new technology were as follows:

- Heavy-duty cleaning power on broad range of industrial soils.
- Compatible with all major metal types including brass.
- Extremely low foam - suitable for high pressure spray.
- No silicates or borates.
- Low level of glycol ether.
- 400 ppm hard water tolerance @ 160°F.
- Low pH < 10.
- Domestic & Foreign registrations ie. TSCA, EINCES, DSL.
- Less than 0.5% Phosphorus content.
- Broad use level range 3% - 20% conc.
- 70°F - 190°F use cleaning temperatures.

The strategy for obtaining a heavy duty cleaning profile in a low pH product was to first maximize the cleaning performance by using organic additives such as surfactants and glycol ethers as opposed to relying heavily on high alkalinity/pH. The next phase of the strategy was to explore synergistic combinations of surfactants and glycol ethers. One major limitation with this strategy was that the final cleaning product must have an extremely low foam profile. Many conventional surfactants with high cleaning profiles are also unfortunately high foamers.

A laboratory, static cleaning test method was first employed to determine the feasibility of different cleaning compositions. The method is as follows:

1. 200 mls of test cleaning solution is stirred in a beaker.
2. Solution is warmed to 50°C using water bath.
3. Magnetic stir bar is set at 150 rpms.
4. Metal coupons (1" X 3") are uniformly soiled with 1.00 gram of test soil (+/- 0.05) and cured in oven.
5. Coupons are placed in beaker and cleaned for a specified time. They are rinsed and dried in oven.

6. After drying, the amount of remaining soil on coupon is determined gravimetrically. Several test soils were selected for use with this method. They were representative of the automotive market. The first was a Heavy Duty Grease. This is a very tenacious and difficult soil to remove. The next was a Petroleum Oil Base Lubricant. Typical of those used on automotive & industrial parts. A Synthetic Grease was also included in the study. This multi purpose grease is commonly used in auto repair shops. The last test soil is commonly referred to as a Corrosion Coating. These are typically oil-based, long-term corrosion inhibitors for metal parts. They protect metals from "flash rusting" after the cleaning process is finished.

In order to interpret the cleaning results it is important to understand whether a particular soil removal score, such as 50%, is considered to be poor, good, or excellent. The following table depicts what levels of soil removal are required for each particular soil to considered poor, good or excellent.

Rating	Heavy Grease	Corrosion Coating	Oil	Synthetic Grease
Poor	< 30	< 30	< 20	< 40
Good	30 - 70	30 - 70	20 - 40	40 - 80
Excellent	> 70	> 70	> 40	> 80

Table 1 – Cleaning Ratings for Industrial Soils Based on Soil Removal (% soil removed after cleaning).

Innovative surfactant blends of different detergent types were explored in search of a synergistic composition that could exhibit high cleaning performance profiles at low pH conditions (pH < 9.5). Many different mixtures of nonionic, anionic, cationic & amphoteric surfactants were evaluated for their feasibility in this application. One particular blend of multiple nonionic and cationic surfactants exhibited an excellent cleaning profile. This surfactant blend was compared to industry standard nonionic surfactants used in the metal cleaning industry. These included NPE-9 (nonoxynol-9), an ethoxylated linear alcohol and a block copolymer. The results of this cleaning evaluation are summarized in Figure 1 below:

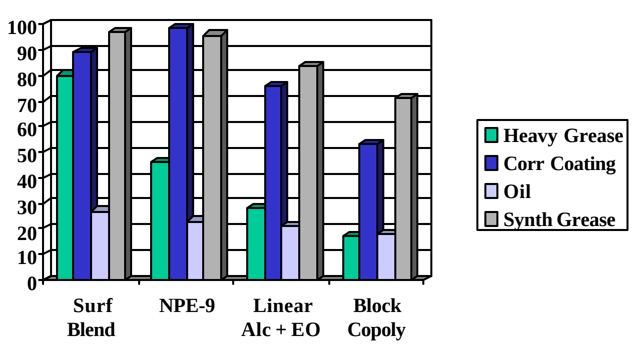

Fig. 1 - Cleaning Comparison (% Soil Removal) of Various Surfactant System Blends

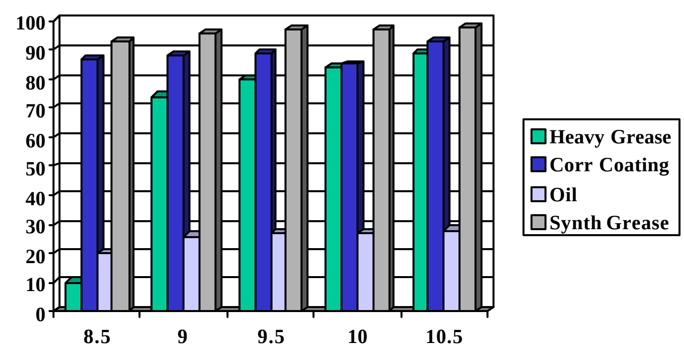

Fig. 2 - Cleaning (% Soil Removal) as a Function of pH

The new surfactant blend cleaned significantly better than all three conventional nonionic surfactants on the Heavy Grease soil. On the Corrosion Coating soil the Surfactant Blend exhibited comparable cleaning to NPE-9 and superior cleaning to the ethoxylated linear alcohol and the block copolymer. All four surfactant systems exhibited comparable cleaning on the Oil. Finally, on the Synthetic Grease the Surfactant Blend exhibited comparable cleaning to NPE-9 and superior cleaning to the ethoxylated alcohol and block copolymer nonionic surfactants. As a result of this study it was decided to proceed with the new surfactant blend as the base detergent system in the new cleaning technology.

One important aspect of this formulation development project was to determine how low the product's pH could be reduced without adversely affecting the surfactant blend's cleaning power. The reason for this action was to improve the environmental friendliness of the product as well as improve its corrosion inhibition properties, particularly on brass and copper. A study was conducted by varying the pH in the range of 8.5 - 10.5 while maintaining a constant total alkalinity in all test solutions. All four test soils described earlier were used in this study. The results are depicted in Figure 2.

Several commercial products were selected for comparative cleaning evaluations. The goal was to select different types of aqueous cleaners to provide a variety of cleaning technologies for comparison. For example it was of interest to select a typical highly alkaline, low foam spray cleaning containing some caustic, silicates, etc. In addition, a manual parts cleaner containing a very high surfactant loading was included. Finally a cleaner with a high solvent, in this case a glycol ether, with a moderate pH (10) was also used for comparison. Descriptions of the three commercial products as well as the New Cleaning Technology are summarized below:

1. Cleaner A - New Cleaning Technology containing synergistic nonionic / anionic surfactant blend, no silicates or phosphates and < 5% glycol ether. pH = 9.5.
2. Cleaner B - Highly alkaline, low foam spray cleaner containing silicates, caustics.
3. Cleaner C - Highly alkaline manual parts / immersion cleaner containing silicates, caustics, high surfactant loading (> 15%)
4. Cleaner D - Moderate pH (10), glycol ether-based formula containing > 15% glycol ether.

The four cleaners differ quite significantly in their physical properties. Some important differences include pH, alkalinity, foam profile, surfactant content and solvent or glycol ether content. These properties are summarized in Table 2 below:

Property	Cleaner A	Cleaner B	Cleaner C	Cleaner D
pH (10%)	9.5	11.1	12.0	10.0
Alkalinity (meq/g)	1.07	0.84	3.02	0.55
Foam in mls (10%)	5	3	60	5
Surfactant Content	< 5%	< 5%	> 15%	< 5%
Glycol Ethers	< 5%	0	0	> 15%

Table 2 - Physical Properties of Commercial Cleaners

A cleaning study comparing the New Cleaning Technology (Cleaner A) to three commercial products was then conducted. The results of this study are depicted in Figure 3 below:

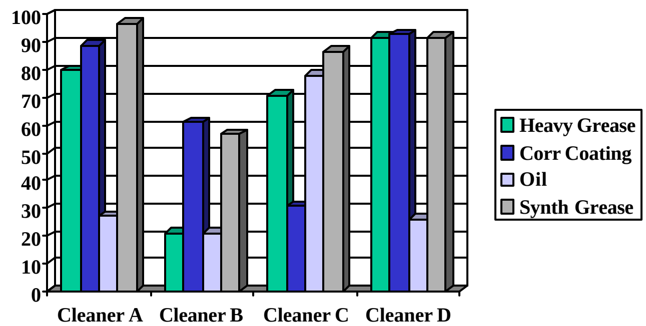

Fig. 3 - Cleaning Comparison of Commercial Products

The results indicate that the New Cleaning Technology exhibited superior cleaning to Cleaner B (Highly alkaline, low pH spray cleaner) on three soils (Heavy Grease, Corrosion Coating & Synthetic Grease) and comparable to Cleaner B on the fourth soil (Oil). This was remarkable since the pH of Cleaner A (9.5) is significantly lower than that of Cleaner B (11.1).

The results also indicate that the New Cleaning Technology exhibited superior cleaning to Cleaner C (Highly alkaline manual parts / immersion cleaner containing silicates, caustics, high surfactant loading > 15%) on two soils (Heavy Grease & Corrosion Coating), comparable to Cleaner C on one soil (Synthetic Grease), and inferior to Cleaner C on one soil (Oil). Overall Cleaner A is considered superior to Cleaner C. The reason Cleaner C is superior to Cleaner A on the Oil is due to its extremely high surfactant content. However, Cleaner C cannot be utilized as a spray cleaner due to its high foam profile (see Table 2) unlike Cleaner A, which functions as both an effective spray and immersion cleaner.

Finally the results indicate that the New Cleaning Technology exhibited comparable cleaning to Cleaner D (Moderate pH (10), glycol ether-based formula containing over 15% glycol ether) on all four soils. The difference here is that Cleaner D contains over 15% glycol ether solvent while Cleaner A has < 5% glycol ether solvent. Cleaner A can use less glycol ether and obtain the same cleaning profile as Cleaner D due to the innovative surfactant blend, which comprises its detergent component.

One of the most important properties that the New Cleaning Technology needed to possess was broad multi-metal compatibility. Most conventional aqueous cleaners rely on inorganic silicates to provide protection on aluminum and steel metal alloys. However the silicate “residue” left on metal parts, which actually provides the metal corrosion protection, is both unsightly and may interfere with post cleaning operations. As a result, an alternate corrosion inhibition technology was explored due to undesirable silicate residues and high pH requirements for to stabilize silicates in an aqueous product.

Organic corrosion inhibition agents were explored as alternatives to conventional inorganic molecules such as silicates. Many functionalized organic molecules adsorb and complex to metal hydroxide surfaces. This organic monolayer physically blocks water molecules from reaching the metal and causing corrosion. Examples include amines, carboxylates, triazoles, etc. Different chain lengths, degrees of ethoxylation or carboxylation, etc. are required for protection of different metals. As a result, extremely complex blends of functionalized organic molecules are required to provide multi-metal protection.

A modified version of ASTM method F483-91 (“Standard Test Method for Total Immersion Corrosion Test for Aircraft Maintenance Chemicals”) was utilized for our corrosion study. This particular evaluation relies on visual changes to rate the degree of corrosion inhibition for a particular aqueous product. This test is conducted in the following manner. Test metal coupons were placed in diluted test cleaners (10%) and then stored in sealed containers at 160°F for one week. These coupons were then rinsed, dried and evaluated visually for rust, darkening or discoloration, staining, etching, pitting and iridescence. Metals included in this study were Aluminum 6061, Copper CA-110, Brass Alloy 260 and Carbon Steel 1010. In addition a standard iron chip corrosion test was also conducted. The results of this study that included all four commercial cleaning products are summarized in the Table below:

Test	Cleaner A	Cleaner B	Cleaner C	Cleaner D
pH	9.5	11.1	12.0	10.0
Iron Chips	0%	0%	0%	0%
Aluminum 6061	Good	Slightly Darkened	Good	Good
Copper CA-110	Good	Good	Good	Darkened –blue water
Brass Alloy 260	Good	Good	Good	Good
Steel 1010	Good	Good	Good	Good

Table 3 - Corrosion Inhibition Comparison

The results of this corrosion study indicate that Cleaner A and Cleaner C were compatible with all five test metals. Cleaner B slightly darkened the Aluminum 6061. Cleaner D darkened the Copper CA-110 metal that resulted in blue colored test water. This phenomenon is due to copper leaching into the water as a result of the Cleaner D. It is apparent from this test that the corrosion inhibition packages in Cleaner B & Cleaner D would benefit from further optimizations.

Another major goal for this New Cleaning Technology was its compatibility and recyclability through ultrafiltration membrane (0.05 micron filter) systems. Ultrafiltration technologies provide an efficient way to remove oils / soils from aqueous cleaning solutions. Eliminating contaminants in this manner to produce clean washing solutions is commonly referred to as “recycling” thus the phrase recyclable cleaner has emerged to describe these types of products. These types of recycling operations adversely affect many conventional aqueous cleaners. The primary cleaning agents, or conventional nonionic surfactants, tend to be removed from the wash solutions along with the contaminant soils. The feasibility of using the New Cleaning Technology with ultrafiltration systems was explored.

The test method utilized to evaluate the cleaning efficacy of the different recycled test products was very straightforward. Test solutions were recycled through a 0.05 micron ultrafiltration system at a typical operating temperature (140°F). The resultant permeates or materials which passed through the membrane were then collected and evaluated for cleaning vs. the original (non-recycled) cleaner.

The New Cleaning Technology was evaluated using all four test soils. The results for this study are summarized in Figure 4 below:

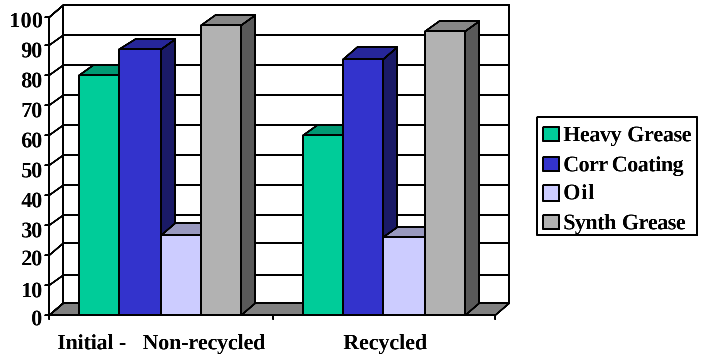

Fig 4 - Cleaning (% Soil Removal) of New Cleaner using Ultrafiltration

The test results indicated that the ultrafiltration process did not significantly affect the cleaning efficacy of the New Cleaning Technology. The cleaning efficacy of the New Cleaning Technology was significantly reduced on one soil (Heavy Grease). However, the resultant cleaning efficacy of the New Cleaner on the Heavy Grease soil after ultrafiltration was still rated as "Good" based on the cleaning scale presented earlier (Table 1).

Pilot cleaning studies was the next logical step in this research program. These studies utilized real world cleaning machines, conditions and metal parts. The first study utilized a high-pressure spray machine. In this test Cleaner A (New Cleaning Technology) and Cleaner B (Highly Alkaline Spray Cleaner) were evaluated in a commercial, top-loading spray wash machine utilizing a polymeric ultrafiltration system for recycling of the aqueous wash solution. The conditions for this test were: 35-psi spray, 160°F temperature, and one-minute spray to make the test difficult. Heavy Grease & Oil were selected as the test soils for this study.

The test procedure was as follows:

1. 4” X 5” steel sheet metal coupons were cut, washed and prepared for testing.
2. One gram of Asphalted Grease soil was evenly spread across each metal coupon and allowed to dry for at least 24 hours.
3. Coupons placed in machine and sprayed with 10% cleaner solutions for one minute at 160°F with no rinse.
4. % Soil Removal was then calculated gravimetrically.

The results of the high-pressure spray pilot testing are depicted below in Figure 5.

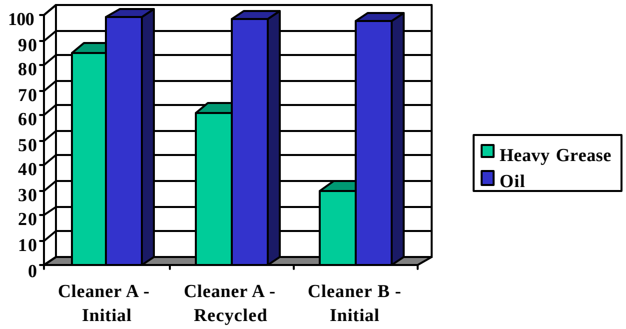

Fig. 5 - High-Pressure Spray Pilot Cleaning Test Results

The results of the ultrafiltration impact of this study were comparable to the laboratory studies. In both cases the New Cleaner's efficacy on Oil was not affected by the ultrafiltration system. However in both cases its efficacy on the Heavy Grease soil was significantly reduced. However, as mentioned earlier the resultant cleaning efficacy of the New Cleaner on the Heavy Grease soil after ultrafiltration was still rated as "Good" based on the cleaning scale presented earlier (Table 1) and significantly better than Cleaner B's non-recycled (initial) efficacy on this soil.

These pilot tests were repeated using a commercial immersion cleaning machine. In this study Cleaner A (New Cleaning Technology) and Cleaner C (Highly alkaline manual parts / immersion cleaner) were evaluated in a commercial, agitated immersion machine utilizing a polymeric ultrafiltration system for recycling of the aqueous wash solution. The conditions for this test were: moderate agitation, 160°F temperature, and one-minute wash to make the test difficult. Heavy Grease & Oil were again selected as the test soils for this study. The results of the immersion pilot testing are depicted below in Figure 6.

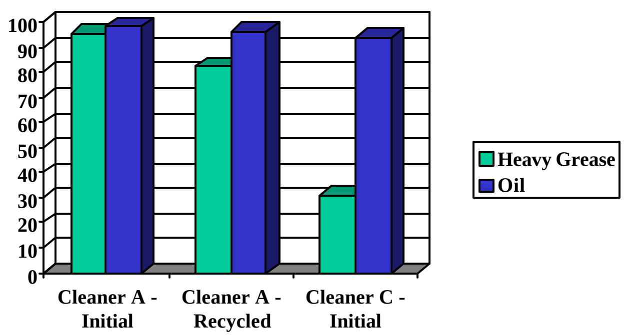

Fig 6 - Immersion Pilot Cleaning Test Results

The conclusions from this immersion cleaning study were exactly the same as the high-pressure spray study. The New Cleaning Technology did not exhibit a change in cleaning efficacy for Oil after ultrafiltration. It did however exhibit a significant reduction in cleaning efficacy for Heavy Grease after ultrafiltration. However, as mentioned earlier the resultant cleaning efficacy of the New Cleaner on the Heavy Grease soil after ultrafiltration was rated this time as "Excellent" based on the cleaning scale presented earlier (Table 1). In addition it was found to be significantly better than Cleaner B's non-recycled (initial) efficacy on this soil, which would be rated as "Poor."

Finally field tests were conducted at customer locations to complete this research program. Fifteen different customer sites in three different geographical locations were selected for the test. Seven utilized high-pressure spray, six utilized immersion cleaning and two utilized mop water applications. Most of the customer's previous cleaners (12) were traditional high pH, silicated products. Two test sites formerly utilized low pH cleaner types and one used mineral spirits. Metal substrates included carbon steel, aluminum, brass & copper.

Comprehensive questionnaires containing 31 different questions were administered at each test site location three times during the course of the field test. Here are the results of some of the key questions.

1. Q. How effective is the cleaner you have been using? (10 - Extremely Effective, 0 - Extremely Ineffective)

   A. 7.0

2. Q. How effective is the New Cleaning Technology? (10 - Extremely Effective, 0 - Extremely Ineffective)

   A. 9.0

Some additional results are summarized in Table 4 below:

Parameter	New Cleaner[1]	Compared to Previous[2]
Corrosion Inhibition	10.0	5.0
Low Residue	9.5	5.0
Low Odor	9.0	7.0
Low Foam	8.5	5.0

Table 4 - Additional Questionnaire Results. [1] 10=Excellent, 0=Poor [2] 5=Similar, 10=Better, 0=Worse

The results of this field test indicate that the Low pH, non-silicated New Cleaning Technology exhibits superior cleaning performance to a variety of previously utilized commercial cleaners. Also the corrosion inhibition, foam & odor were found to be at least equal to previous products including silicated products on steel & aluminum castings. And finally the controlled field test confirmed the results of lab and pilot evaluations - that a low pH (< 9.5), non-silicated product can provide excellent, well-rounded cleaning & recycling performance in the real world.