

CHEMICAL SUBSTITUTION FOR 1,1,1-TRICHLOROETHANE AND METHANOL
IN MANUFACTURING OPERATIONS

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ABSTRACT

Hazardous wastes are generated from cold solvent degreasing operations used in many industrial processes. The spent solvents are managed under Subtitle C of the Resource Conservation and Recovery Act (RCRA). With the land ban of spent solvents, disposal has become increasingly difficult. As a result, industries began investigating ways to avoid using RCRA listed cleaning solvents. EPA's Pollution Prevention Research Branch along with APS Materials, Inc., a small metal finishing company, participated in a joint research project to evaluate the substitution of a dilute, terpene-based cleaner for 1,1,1-trichloroethane (TCA) and methanol, hazardous wastes F001 and F003 respectively, in their degreasing operations.

This paper presents the results of a study evaluating the waste reduction/pollution prevention that can be achieved by substituting dilute limonene solutions for TCA and methanol in the cleaning of orthopedic implants (e.g. metal knee and hip replacements). This paper describes the original cleaning process, the modifications made to the process in using the dilute limonene solution, and the sampling plan used in evaluating the effectiveness of the solution. The paper presents qualitative results of the sampling tests and an economic evaluation of plant modifications.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names of commercial products does not constitute endorsement or recommendation for use.

INTRODUCTION

Passage of the 1984 Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) of 1976 has redirected the U.S. environmental policy towards waste minimization to improve the quality of the environment. In its efforts to pursue the objectives set forth by Congress in the HSWAs to RCRA, the USEPA has established a national comprehensive pollution prevention program that includes information gathering, research and development, demonstration, support of state and local government pollution prevention programs, training and education, technology transfer activities, pollution prevention assessments, and extensive communications with universities and the general public. Implementation of programs to achieve several of these objectives is accomplished through research conducted by the Pollution Prevention Research Branch of the Risk Reduction Engineering Laboratory. This research addresses the intent of the Amendments to reduce the release and transport of hazardous, toxic, and nonhazardous materials through the air, water and solid media. The research is of significant benefit to the USEPA, states, waste generators, and the general public since results of this research will assist in reducing the generation of pollutants that threaten both public health and the environment. The principal goal of the Pollution Prevention Research Branch is to encourage the identification, development, and demonstration of processes and techniques that result in less waste being generated in order to promote a more rapid introduction of effective pollution prevention techniques into broad commercial practice.

1,1,1-trichloroethane (TCA) is used as a cold solvent degreasing agent in many industrial degreasing processes. In 1986, (TCA) was identified as a hazardous waste that must be managed under Subtitle C of the Resource Conservation and Recovery Act. As a result of this action, industries began looking for ways to avoid the use of TCA cleaning solvents. The EPA decided to target the metal finishing industry for participation in a joint research project to examine the possibility of substituting a terpene-based cleaner for TCA in degreasing operations. APS Materials, Inc., a facility in Dayton, Ohio participated in the research project. APS Materials, Inc. is a metal parts finishing company which generates TCA and methanol waste from cold solvent degreasing operations associated with their plasma spray deposition process.

PLASMA SPRAY DEPOSITION PROCESS

The plasma spray deposition process has emerged as a major means to apply a wide range of materials on diverse substrates. The deposition process is accomplished with the use of a plasma gun. In the plasma gun, an electric arc is formed between positive and negative electrodes via an electric discharge initiated by direct current. The discharge gives rise to a breakdown of the dielectric nature of the gas, making it conductive. The net result is a gaseous collection of energetic electrons and ionized molecules known as a plasma. The plasma exits as a high velocity flame through the nozzle of the gun. A powdered feedstock is injected into the flame via a carrier gas (usually argon). The injected powder accelerates, melts, and is carried at sonic velocities to the substrate on which the particles impact and solidify rapidly, at rates about one million degrees per second, building a well adhered protective coating. (1)

While APS Materials, Inc. employs the fundamental plasma spray deposition process, a few changes were made to better accommodate the plasma spray work performed by their company. First, APS Materials performs its plasma spraying in an inert atmosphere chamber. This is done for cooling and to prevent the titanium powder used in many of its coating applications from becoming oxidized thus forming brittle coatings. APS Materials also uses helium in the spray gun as a mix gas and to adjust the heat level and arc length.

Typically, the plasma spray deposition process requires only a small amount of substrate preparation. However, because APS Materials is involved in plasma spraying parts that must perform in such hostile environments as aircraft engines (aircraft parts) and the human body (orthopedic implants), they must be assured that the plasma sprayed coating is securely adhered to the substrate. For this reason, parts that arrive at APS for coating undergo a thorough cleaning process prior to the application of the plasma spray coat.

PROCESS DESCRIPTION

ORIGINAL PROCESS

In the APS biomedical parts division, the company primarily coats cobalt/molybdenum parts and titanium parts with a porous titanium alloy. By using plasma spray technology, the porosity of the coating is controlled so that growing bone will attach to the metal surface. In order to achieve a strong and adhesive coating, the parts were cleaned with TCA or methanol (TCA for cobalt/molybdenum and methanol for titanium). TCA is more economical than methanol but weakens titanium over time. The cleaning process consists of several steps. Initially, the parts

received undergo a visual inspection for any gross defects. The parts are then partially masked with tape, exposing only the surfaces that will receive spray coating. Next, they are grit blasted to roughen the surface of the part for the application of the spray coat. After the grit blast has been completed, the masking tape is removed. The part is then immersed in a small pail containing TCA or methanol. The pail is placed in an ultrasonic bath containing warm water for 15 minutes. Solids from grit blasting, oil and grease from the manufacturing and handling of the parts, and any adhesive residuals from the masking tape are removed in this cleaning process. After the ultrasonic bath, a graphite masking suspension is applied to the part on surfaces where the plasma spray coating is not wanted. The part is then plasma sprayed and cleaned again to remove excess titanium and the graphite mask.

As a check system, APS runs small one inch diameter disks of the same composition as the part to be coated - called "test buttons" - through the same cleaning and coating process. The test buttons are placed on a tensile strength testing machine which measures the tension required to separate the coating from the substrate as a quality control measure.

Many wastes are generated during the preparation of the part for spray coating, with TCA and methanol being the wastes of primary concern. Waste TCA and methanol were being generated at the rate of 1/2 barrel per month each. Disposal of these solvents was becoming more and more difficult.

DESCRIPTION OF INITIAL BENCH SCALE EXPERIMENTS

DuSqueeze, a product of DuBois Chemicals, was selected as a possible substitute for TCA and methanol because of its disposal qualities. Disposal of dilute solutions of DuSqueeze could be accomplished by flushing it to a sanitary or industrial sewer according to local sewer use permit requirements. The feasibility of substituting a dilute, terpene-based cleaner (DuSqueeze) for TCA and methanol was determined by assessing the tensile strength of the plasma coating bonds made after cleaning with DuSqueeze. Five tests were performed, four on plasma coated test buttons to assess the tensile strength of bonds made after cleaning with DuSqueeze as compared to the tensile strength of bonds made after cleaning with methanol and TCA, and one test to determine if any limonene remained on the buttons after being cleaned. In the first test, four titanium test buttons were placed in a stainless steel beaker containing a 20:1 dilute solution of DuSqueeze and water. The solution was agitated for 20 seconds. The test buttons were then placed in a stainless steel beaker containing deionized (DI) water which was agitated for 20 seconds. The test buttons were then blow-dried and plasma sprayed. The tensile strength of the bond between the plasma arc coating and the substrate was measured using a Tinius Olsen tensile tester.

In the second test, four titanium buttons were placed in an ultrasound bath containing a 50:1 dilute solution of DuSqueeze for 10 minutes. Next the buttons were placed in a stainless steel beaker containing DI water for thirty seconds. The titanium buttons were blow dried for sixty seconds and then plasma sprayed. The tensile strength of the bonds were then tested in the same manner as the first test. The third test followed the same procedure as test two, using a 100:1 dilute solution of DuSqueeze. In the fourth test the buttons were cleaned by the same process as the third test, but the buttons were analyzed for residual limonene and were not plasma sprayed and tensile tested. In the fifth test, cobalt/molybdenum buttons were used instead of the titanium buttons with the test protocol identical to the third test.

MODIFICATIONS TO EXISTING SYSTEM

APS purchased a heated ultrasound bath with a timer for the conversion. However, when this ultrasound bath malfunctioned, a heater was added to the old ultrasound bath. The TCA/methanol cleaning system did not require a DI water rinse, so a DI water system was purchased along with a stainless steel bath and immersion heater. With the new cleaning system, the parts take longer to dry, so a heat gun was purchased to speed-up the drying process.

SAMPLING AND ANALYSIS

The overall purpose of the sampling and analysis project at APS Materials was to support a purely qualitative judgement of the cleaning capabilities of the substitute cleaning solution (i.e., DuSqueeze). The sampling and analysis protocol for this project was set up in three parts; sampling spent solutions of methanol and TCA, sampling the terpene-based cleaning solution after modifications were made to the cleaning system, and developing data for a comparative analysis of plasma coating bond strengths between the coatings of test buttons that were cleaned with methanol/TCA prior to coating and the coatings of test buttons that were cleaned with the terpene-based solution prior to coating.

PRE-MODIFICATION SAMPLING

The first part of the sampling process was performed prior to any modifications. This sampling was performed in order to determine the type and amounts of contaminants found in the cleaning solvents. Samples of the methanol and TCA cleaning solutions were taken and analyzed for oil and grease, dissolved solids, suspended solids, titanium metal and cobalt metal. This sampling also established the baseline performance for methanol and TCA. The samples were taken by mixing the material in a plastic bucket and then pouring a sample from the bucket through

a glass funnel into a glass bottle. The data derived from this sampling served as a bench mark for the ensuing DuSqueeze sampling.

POST-MODIFICATION SAMPLING

The second part of the sampling scheme was performed after the modifications were made to the system in order to determine the effectiveness of the terpene-based solvent (DuSqueeze) in cleaning the parts. Sampling of the cleaning solution was performed throughout a typical operating cycle. Samples were recovered at the beginning of a bath cycle (i.e., when the tank contents were completely replaced with fresh cleaning solution) to establish baseline concentrations. A second sample was taken midway through the effective life of the cleaning solution. A final sample was recovered prior to removing the spent solution from the dip tank.

One liquid sample was collected during each sampling episode and split into two aliquots. One aliquot was placed in a 1000-ml linear polyethylene bottle with a screw-cap lid. This sample was used to analyze for dissolved/suspended solids and the two specific metals. The second aliquot was used to test for oil and grease and was placed in a 1000-ml glass bottle with screw-cap lid. Before use, the sample containers were soap-and-water washed, rinsed thoroughly, and then soaked in acid (nitric acid for plastic, sulfuric acid for glass) for several hours. The bottles were then rinsed thoroughly with tap water, distilled water, and deionized distilled water respectively. They were air-dried and stored with their caps in place.

Preservation procedures were performed on the liquid samples immediately after sample collection. The pH of each liquid sample was measured using pH indicator paper. Acid was added to each sample until the pH was reduced to 2.0. The samples that were analyzed for dissolved/suspended solids and metals were pH-adjusted using nitric acid. Sulfuric acid was used for preserving the oil and grease samples.

In addition to taking samples of the cleaning solution, wipe samples were taken of the cleaned parts. Wipe samples were taken to evaluate the cleaning efficiency of the solution over time by analyzing for residual contaminants (oil and grease) on the parts. One wipe sample was taken from the cleaned metal parts during each sampling interval to determine if there was a residual of oil and grease. The wipe sample was performed using sterile, uncontaminated cloth. Sterile gloves were worn to prevent contamination of the cloth with oil and grease. The wiping procedure was consistent for each sample. A glass container of sufficient volume was used to hold the cloth after sampling. Three wipe samples were taken over the life of the DuSqueeze cleaning solution, to coincide with the three liquid samples described above.

Analysis for metals was performed using inductively-coupled plasma atomic emission spectroscopy (ICP). Oil, grease and dissolved/suspended solids were analyzed using gravimetric analytical techniques. Spikes and replicate analyses were also done to check for accuracy and precision and to identify the presence of any matrix effects associated with sample preparation or measurement. Data were then combined and statistically evaluated.

The analysis of plasma coating bond strength compared current data collected by APS Materials regarding the strength of coatings applied after parts were cleaned with DuSqueeze and historical data of bond strength resulting from parts cleaning with TCA and methanol. Data generated two months prior and two months following the conversion to DuSqueeze was used for this comparison.

RESULTS AND DISCUSSION

BENCH SCALE EXPERIMENTS

The before and after tensile strength results were comparable. Overall, the bonding strengths were actually slightly better for the dilute limonene cleaner (see Table 1). No residual limonene was detected (detection limit 1 ppm) for cleaner at 100:1 dilution.

TABLE 1. TENSILE STRENGTH TEST RESULTS FOR BENCH SCALE EXPERIMENTS

Test Buttons	Cleaning Agent	Tensile Strength (psi)
titanium	methanol	6300+/-1260
titanium	DuSqueeze*	7000+/-570
cobalt/molybdenum	TCA	5150+/-1990
cobalt/molybdenum	DuSqueeze*	5400+/-1290

* Tensile strengths measured for test button cleaned with various dilutions of DuSqueeze showed no trends or statistical differences, so values shown include all measurements.

ANALYSES FOR IN-PLANT OPERATIONS

The initial tests for contaminants in methanol and TCA used for cleaning yielded the results shown in Table 2. The samples for these analyses were taken when the baths were considered spent, just prior to being dumped.

TABLE 2. RESULTS OF ANALYSES OF SOLVENT SAMPLES FOR CONTAMINANTS

Test	Methanol (mg/l)	TCA (mg/l)
Dissolved solids	1	29
Suspended solids	33	9
Oil and Grease	911	141
Metals		
Cobalt	-	ND
Titanium	0.021	-

* Method detection limit is 0.01

The amounts of oil and grease found in the wipe samples, shown in Table 3, were very low at about 1 mg or less. The increase in oil and grease from the bath dump as compared to the fresh bath was very small for one sample and was less than the fresh bath in the second bath dump sample. This latter result could have resulted from the wiping technique. In any case, the parts seem to be cleaned just as well at the time the bath is dumped as when the bath is fresh.

TABLE 3. RESULTS OF ANALYSES FOR OIL & GREASE ON PARTS CLEANED WITH 100:1 DILUTE SOLUTION DUSQUEEZE

Test	Oil and Grease Total Mg
Wipe Sample, Fresh Bath	1.0
Wipe Sample, Mid-life Bath	0.4
Wipe Sample, End-life Bath	1.2
BLANK	ND*

* Method detection limit is 0.3

Table 4 shows results from analyses for residual limonene on the parts. Limonene was not detected in the rinse samples, thus indicating that all of the limonene was removed during dragout and subsequent drying of the parts.

TABLE 4. RESULTS OF ANALYSES FOR RESIDUAL LIMONENE ON PARTS CLEANED WITH 100:1 DILUTE SOLUTION DUSQUEEZE

Test	limonene concentration Total Ug/sample
Rinse Sample, Fresh Bath	ND(<0.3)
Rinse Sample, Mid-life Bath	ND(<0.65)
Rinse Sample, End-life Bath	ND(<0.3)
BLANK	ND(<0.2)

In comparing the results in Table 5, it is noted that dissolved solids and oil and grease were much higher in the fresh bath and the bath used to clean parts only prior to plasma spraying (Dump#1), than in the bath used also for cleaning after plasma spraying (Dump#2), while the reverse was true for the suspended solids. The graphite in the bath may affect the DuSqueeze cleaning solution to create these differences.

TABLE 5. RESULTS OF ANALYSES OF 100:1 DULUTE DUSQUEEZE SOLUTION FOR CONTAMINANTS

Test	Fresh Bath	Dump#1	Dump#2
Dissolved solids	3650	3010	887
Suspended solids	ND*	ND*	19
Oil and Grease	37.0	30.8	15.1
Metals			
Cobalt	0.019	0.18	0.081
Titanium	ND#	ND#	1.65

* Method detection limit is 2

Method detection limit is 0.047

In comparing the DuSqueeze cleaning solution with the previous methanol and TCA samples, it is noted that the oil and grease levels in the DuSqueeze are much lower than the other cleaning solvents. Suspended solids for the DuSqueeze are lower than the previous solvents except for the sample containing graphite which is roughly equivalent. Dissolved solids for DuSqueeze are much higher than the other solvents.

The higher dissolved solids may reflect the fact that the DuSqueeze is an emulsifying agent which converts the oil and grease to dissolved solids. This would explain the lower oil and grease levels for DuSqueeze.

TABLE 6. TENSILE STRENGTH TEST RESULTS FOR IN-PLANT OPERATIONS

Coating/Substrate	Cleaning Agent	Tensile Strength
titanium / titanium	methanol	5560+/-600
titanium / titanium	DuSqueeze	7180+/-610
titanium / cobalt-moly	TCA	5820+/-370
titanium / cobalt-moly	DuSqueeze	5330+/-1560

Although the data generated by the sampling and analysis program, shown in Table 6, indicates that the terpene-based cleaner adequately cleaned the parts for this process, since wipe samples were not taken for the original process, a statement of comparison between the former and present cleaning techniques is not feasible.

ECONOMIC ANALYSIS

Although the old ultrasound bath was in use at the time of the test, economic analysis is shown for the system that APS is now operating.

- Capital Cost: Ultrasound with heater \$1425
 5 gallon stainless rinse vessel \$38
 Immersion heater \$105
 Heat Gun \$75
 DI water system installation \$150
 TOTAL - \$1793
- Annual operating costs: 7.8-11.8 gal DuSqueeze \$150
 1825-2920 gal DI water \$700
- Cost savings from avoided purchases:
 330 gal TCA \$1650
 120 gal methanol \$1000
- Cost savings from avoided disposal: 6 barrels \$3000
- Net Cost savings: \$4800 a year
- Payback \$1793/\$4800 = 0.37 year, 4.5 months

CONCLUSIONS

In summary, it has been determined that a terpene-based cleaner can adequately clean metal parts without adversely affecting the performance of the plasma-arc coating application. The use of a terpene-based cleaner in place of methanol and TCA has proven to be an environmental and economic success. Elimination of the disposal problems associated with methanol and TCA coupled with the maintenance of plasma-arc coating quality makes the use of terpene-based cleaners attractive to other plasma spray coating processes as well as other metal cleaning/coating operations. The annual cost savings as well as the short payback period also make the cleaner attractive from an economic standpoint.

REFERENCES

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