CLEANING LABORATORY EVALUATION SUMMARY

SCL #:	1994
DateRun:	12/14/1994
Experimenters:	Donald Garlotta, John Bulko
ClientType:	Cleaner Manufacturer
ProjectNumber:	Project #1
Substrates:	Aluminum, Stainless Steel
PartType:	Part
Contaminants:	Adhesive
Cleaning Methods:	Ultrasonics
Analytical Methods:	
Purpose:	Final Report for Adhesive cleaning

Experimental Procedure:

ITW Adhesive Systems currently manufacturers adhesive products for product assembly, plant maintenance and field service applications which are classified under SIC codes 2821 and 2891. The adhesive products typically consist of two parts, an initiator component (A) and an adhesive component (B). In turn, each of these components is a mixture of resins and other ingredients which impart the desired characteristics to the final adhesive material upon mixing at the time of use. In this study, component A is an organic peroxide solution containing benzoyl peroxide and butyl benzyl phthalate among other additives and is referred to as A0420 ACTIVATOR (aka A0421). Component B ia a methacrylate ester solution the bulk of which is methyl methacrylate and methacrylic acid and is listed as A0420 ADHESIVE. A second set of activator and adhesive components designated MA300 ACTIVATOR and MA300 ADHESIVE containing mostly methyl methacrylate are also included.

Equipment and parts used in formulating and mixing batch quantities of these materials have been cleaned by soaking in methyl ethyl ketone solvent accompanied with manual brushing. U-blades used for batch mixing and shear and pump blades are made of 304 stainless steel while filter flanges are type 6061-T4 aluminum. ITW has requested assistance with:
Identifying an alternative cleaning process to replace the use of methyl ethyl ketone in their cleaning operations, evaluating the performance of SHIPSHAPE (N-methyl pyrrolidone) solvent cleaner as an alternative.
All surfaces in contact with either component must be cleaned sufficiently after each batch so as not to compromise subsequent batch purity and formulation operations nor cause premature free radical polymerization of the methyl methacrylate adhesive.

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Based upon results gathered at ITW concerning substitute cleaning chemistries tried in place of methyl ethyl ketone, it was disclosed that DOWANOL™ PM GLYCOL ETHER (propylene glycol monmethylether)[Dow Chemical] was partially effective in removing the activator and adhesive components from metal surfaces. However, this material did leave behind a residue which was unacceptable. In addition, this product was considered highly flammable, with a flash point of 90°F, and possessed other undesirable health hazard concerns such as a 100ppm TWA OSHA exposure limit.

Using this knowledge, seven aqueous cleaning products were selected for the first round of cleaning trials using A0420 ADHESIVE resin as the contaminant. Speculating that the glycol ether may be an essential ingredient of a successful cleaning formulation, seven candidate cleaners listed in TABLE 1 possessing a glycol ether content between 0-20% were evaluated using an agitated immersion /soak cleaning process.

Results:

Aqueous cleaning chemistries were evaluated for removing adhesive resin compounds from 304 stainless steel and 6061-T4 aluminum mixing and formulation equipment parts. Both initiator and adhesive materials were removed using an agitated immersion soak and brushing process with MacDermid New Dimensions Supreme as the aqueous cleaner at concentrations of 10 and 20 percent between 70°-151°F.

SCOPE and APPLICATION

APPROXIMATE GLYCOL			
PRODUCT	MANUFACTURER	ETHER CONTENT %	TYPE
DARACLEAN 282	WR Grace	3	E
DARACLEAN 282GF	WR Grace	0	-
FISAN VERSACLEAN	Oakite	<20	P,H
	CRC	10-20	P

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COMPLEX BLUEa			
CITRIDET	Oakite	10-20	H
AC 8015	Calgon-Vestal	<15	P
NEW DIMENSIONS SUPREME	MacDermid	4-8	P

TYPE: E = Ethylene-based; P = Propylene-based; H = Hexylene Glycol.

COMPLEX BLUE cleaner was used as delivered from the spray container undiluted at 77°F and left in contact with the contaminated coupon for 60 minutes.

Clean test coupons of 304 stainless steel were contaminated with approximately 50mg of adhesive resin and individually treated using a 10% solution of each cleaner stirred and heated via magnetic stirrer/hot plate. After 15 minutes of agitated soak in the cleaner at temperatures between 138-151°F, two cleaning products were effective in removing 99.6% (New Dimensions Supreme) and 98.4% (AC 8015) of the applied resin. All other products in TABLE 1 left a majority of the adhesive on the coupons at the end of the soak period. Further testing using these two products was continued. Multiple coupon testing of the AC 8015 product revealed the presence of small amounts of oily residue remaining on the 304 stainless steel surfaces after cleaning. In contrast, cleaning with the New Dimensions Supreme product was residue and stain-free. Based upon these results, the Calgon-Vestal AC 8015 product was eliminated from further consideration.

At the request of ITW, testing of aqueous cleaning products was continued using solutions at room temperature and the four most effective products of those shown in TABLE 1 accompanied by the added factor of manual brushing. The current cleaning operation using methyl ethyl ketone does include manual brushing of parts after a period of soaking. Stainless steel coupons were contaminated with A0420 ADHESIVE and placed in a one-liter agitated solution containing 10% (by volume) cleaning product for either a 15 or 30 minute period followed by manual brushing with a standard nylon test tube brush upon removal from the solution. Results are shown in TABLE 2.

TABLE 2.			
CLEANING PRODUCT	SOAK PERIOD	TEMP. °F	BRUSHING TIME REQUIRED TO REMOVE ALL ADHESIVE RESIN
DARACLEAN 282GF	15 min	80	15 sec
FISAN VERSACLEAN	15 min	80	15 sec
CITRIDET	15 min	80	30 sec
ND SUPREME	15 min	80	30 sec
FISAN VERSACLEAN	30 min	80	60 sec
CITRIDET	30 min	80	30 sec
DARACLEAN 282GF	30 min	80	30 sec

The A0420 ADHESIVE was removed completely by all four cleaning products with the assistance of brushing.

A similar series of experiments was performed using test coupons of aluminum 6061-T4 contaminated with A0420 ADHESIVE to evaluate the compatibility of the cleaning chemistries with the other metal used in equipment and parts at ITW. Results are compiled in TABLE 3 below.

TABLE 3.			
CLEANING PRODUCT	SOAK PERIOD	TEMP. °F	BRUSHING TIME REQUIRED TO REMOVE ALL ADHESIVE RESIN
ND SUPREME	15 min	86	15 sec
DARACLEAN 282GF	15 min	86	20 sec
CITRIDET	15 min	86	8 sec
FISAN VERSACLEAN	15 min	86	5 sec

Based on visual examination, the four cleaning solutions had no deleterious effects on the aluminum coupons.

The second round of cleaning trials was conducted using the A0421 ACTIVATOR compound as the contaminant. Agitated soaking at temperatures between 75°-140°F for up to 30 minutes followed by for 60 seconds left both 304 stainless steel and 6061-T4 aluminum test coupons only partially clean (85%-98%) using a 10% solution of New Dimensions Supreme cleaner. Cleaning experiments using 10% solutions of

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Fisan Versaclean, Citridet and Daraclean 282GF at temperatures between 136°-140°F also left the test substrates only partially clean after 40 seconds of brushing. The Fisan Versaclean solution adversly affected the aluminum, causing surface significant surface discoloration and etching where the cleaner had come in contact with the coupon.

Since the activator was only partially cleaned using a cleaner concentration of 10%, further evaluations were performed using a 20% concentration of New Dimensions Supreme. Testing results are charted in TABLE 4. As indicated, agitated soaking of stainless-steel coupons for up to 45 minutes at temperatures up to 122°F when followed by 60 seconds of brushing with a nylon brush left behind varying amounts of activator residue. Additional soak time under agitation followed by more brushing resulted in the removal of all bulk activator compound but the presence of a residual surface film over the area where the A0421 was originally put. When the temperature of the cleaning solution was raised to 141°F, a 30-minute initial soak with 60 seconds of brushing followed by a second 5-minute immersion at 144°F and 15 seconds brushing did effectively remove the activator and residual surface film completely from the 304 stainless steel substrates. Using these conditions, a contaminated 6061-T4 aluminum coupon was completely cleaned after a 30-minute agitated soak at 142°F and 5 second brush period.

ITW also requested cleaning performance data when contaminated surfaces containing both activator and adhesive materials are present in the same cleaning solution at the same time. Side-by-side testing of the A0420 and A0421 contaminated 304 stainless steel coupons was performed using a one-liter solution of 20% New Dimensions Supreme agitated via magnetic stirrer/hot plate. A coupon spotted with each material was immersed for 15 minutes at 143°F. While still submerged, the adhesive component was removed after 3 seconds of brushing whereas the activator required 30 seconds of brushing to completely remove it.

TABLE 4.							
AGITATED SOAK IN HEATED/STIRRED BEAKER							
CONTAMINANT:	A0421 ACTIVATOR						
CLEANING SOLUTION:	20% NEW DIMENSIONS SUPREME						
Substrate	304 SS						
TEST	INITIAL	TEMP.	BRUSHING		ADDITIONAL	ADDITIONAL	
CPN	SOAK TIME	TIME	RESULTS		SOAK TIME	BRUSH TIME	OBSERVATIONS
#	min.	°F	sec.		min.	sec.	
5	15	75	60	residue remaining	41	15	film residue
22	30	75	60	residue remaining	28	5	film residue
11	45	75	40	residue remaining	14	0	film residue
20	15	120	60	residue remaining	32	10	film residue
13	30	122	60	residue remaining	17	10	film residue
4	45	122	60	residue remaining	5	5	film residue
26	30	141	60	residue remaining	5(144°F) 15	CLEAN	
CONTAMINANT:	A0421 ACTIVATOR						
6061-T4 ALUMINUM COUPONS							
22	30	142	5	CLEAN			

The last group of cleaning trials was performed using another set of activator and adhesive compounds with different composition. These new contaminants were designated MA300 ACTIVATOR and MA300 ADHESIVE, both containing methyl methacrylate as the major component. Side-by side testing of 6061-T4 aluminum coupons spotted with each material revealed that agitated immersion in a 20% solution of New Dimensions Supreme at 71°F for 15 minutes followed by 20 seconds of brushing while the coupons were still submerged was effective in removing both applied resins. It is important to note that both activator and adhesive materials became rubbery in texture, indicating the commencement of polymerization. similar side-by-side cleaning experiments using 304 stainless steel substrates and the same conditions as above lead to effective removal of activator and adhesive after brushing while submerged for 20 seconds and 25 seconds, respectively. Repeating the procedure using the cleaning solution at 140°F after a similar agitated soak required 15 seconds to remove the MA300 ADHESIVE and 90 seconds to remove the MA300 ACTIVATOR. It was apparent that the higher temperature of the cleaning solution, 141°F, required a longer brush time to remove the MA300 ACTIVATOR due to excessive smearing over the surface and the increased degree of polymerization caused by the increased temperature. Agitated soak cleaning using 10% New Dimensions Supreme was effective in cleaning the MA300 ADHESIVE resin from the steel and aluminum substrates except where the adhesive had polymerized to a "plastic-like" texture. Cleaning time (amount of brushing required) however was significantly longer compared to the results using the 20 % cleaner

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concentration. Cleaning of the MA300 ACTIVATOR from both metals was especially problematic using the lower concentration at elevated temperatures due to resin polymerization.

As an alternative to the aqueous cleaning chemistries used above, one cleaning experiment was performed using another class of cleaning product. As indicated by the SOLVENT ALTERNATIVES GUIDE [SAGE] database, N-methyl pyrrolidone was ranked as a possible cleaning alternative. A product call SHIPSHAPE, consisting of essentially N-methyl pyrrolidone, was evaluated for removing the A0420 ADHESIVE resin material. Agitated soak for 30 minutes at 80°F removed approximately 43% of the applied resin. Concerns with safety, health and disposal issues along with inferior performance when compared to aqueous alternatives eliminated this product from further consideration.

The initial premise that the cleaning medium contain glycol ethers as part of an effective formulation was not borne out by the cleaning tests performed here. Although the product performing the best under the stated conditions, New Dimensions Supreme by MacDermid, did contain 4-8% by weight dipropylene glycol methyl ether, a glycol-free product was also found to be effective in removing the A0420 ADHESIVE material and moderately successful in removing the A0421 ACTIVATOR. Further evaluation of Daraclean 282GF (WR Grace) should be done if the presence of glycol ethers in the cleaner formulation is undesirable. Besides the glycol ethers, New Dimensions Supreme contains mild surfactants, emulsifiers and a corrosion inhibitor. It does not contain any chlorinated solvents or petroleum distillates and is non-flammable.

Summary:

Substrates:	Aluminum, Stainless Steel				
Contaminants:	Adhesive				
Company Name:	**Product Name:**	**Conc.:**	**Efficiency:**	**Effective:**	**Observations:**
Magnaflux	Daraclean 282 GF	15	0.00	☐	
Oakite Products	Fisan Versaclean	15	0.00	☐	
MacDermid Industrial Products	ND Supreme	15	0.00	☑	
Oakite Products	Citradet	15	0.00	☐	

Conclusion:

In summary, New Dimensions Supreme was found to be the most effective cleaner for removing methacrylate-based adhesive and activator compounds from 304 stainless steel and 6061-T4 aluminum surfaces. Concentration of the cleaning solution did vary between 10-20% depending on the residue being removed. Temperature of the cleaning medium was varied over the range between room temperature and 144°F. The A0420 ADHESIVE was removed at room temperature while the A0421 ACTIVATOR became easier to remove as the temperature increased. For the MA300 ACTIVATOR, this trend was reversed with removal being easier after room temperature contact with the cleaner. All cleaning experiments did require manual brushing to clean the metal surfaces. Brushing times were significantly shortened and cleaning more effective when surfaces were completely submerged in the cleaning solution during the brushing step. Side-by-side cleaning tests where both activator and adhesive components were present in the same cleaner did not pose any significant problems in removing either residue from aluminum or stainless-steel test coupons. Finally, based on visual examination of the cleaned metal surfaces, there were no noticeable effects observed on steel parts after immersion in 10% New Dimensions Supreme for 116 hours at room temperature or aluminum substrates soaked in 20% cleaner solution for 35 minutes at 144°F.