

SANDIA REPORT

SAND2013-6670
Unlimited Release
August 2013

Critical Cleaning Agents for Di-2-ethylhexyl Sebacate

Mya T. Hartley, Kim M. Archuleta

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.



Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: <http://www.osti.gov/bridge>

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd.
Springfield, VA 22161

Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: <http://www.ntis.gov/help/ordermethods.asp?loc=7-4-0#online>



SAND2013-6670
Unlimited Release
August 2013

Critical Cleaning Agents for Di-2-ethylhexyl Sebacate

Mya T. Hartley, Kim M. Archuleta
Coatings and Surface Engineering Department
Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185-MS0889

Abstract

It is required that Di-2-ethylhexyl Sebacate oil, also commonly known as Dioctyl Sebacate oil, be thoroughly removed from certain metals, in this case stainless steel parts with narrow, enclosed spaces. Dioctyl Sebacate oil is a synthetic oil with a low compressibility. As such, it is ideally used for high pressure calibrations. The current method to remove the Dioctyl Sebacate from stainless steel parts with narrow, enclosed spaces is a labor-intensive, multi-step process, including a detergent clean, a deionized (DI) water rinse, and several solvent rinses, to achieve a nonvolatile residue of ≤ 0.04 mg per 50 mL rinse effluent. This study was undertaken to determine a superior detergent/solvent cleaning method for the oil to reduce cleaning time and/or the amount of detergent/solvent used. It was determined that while some detergent clean the oil off the metal better than the current procedure, using only solvents obtained the best result. In addition, it can be inferred, based on elevated temperature test results, that raising the temperature of the oil-contaminated stainless steel parts to approximately 50°C will provide for improved cleaning efficacy.

ACKNOWLEDGMENTS

Special thanks to Richard Quintana and Walter Olson for assistance in this study and Deidre Hirschfeld and Cher Porter for assistance in the editing and formatting of this SAND report.

Contents

Tables	4
Figures.....	5
I. Introduction	6
II. Experimental	8
III. Test Results and Discussion.....	12
IV. References.....	13

Tables

1. Cleaning Agent Predictor List	8
2. Test Schematic	10
3. Test Results.....	12

Figures

Figure 1 – Hansen Parameters in 3-Dimensional Space.....	7
Figure 2 – SS Coupons Used for Testing.....	9

I. INTRODUCTION

Pressure transducers used for oil-free pressure sensing applications are calibrated with Dioctyl Sebacate oil at the Sandia-Albuquerque Primary Standards Lab. After calibration the oil must be removed completely from the semi-enclosed wetted space of the transducer prior to use. Currently, cleaning the transducers involves a soak and brush in warm Brulin 815GD™ (Brulin), a rinse with DI water, and then an extensive rinse with ethanol using a hand-held squirt bottle. This process is long and meticulous, taking several hours to clean and verify cleanliness level using nonvolatile residue testing. The development of a more efficient cleaning method will result in added value through cost and time savings.

In 1936, Joel H. Hildebrand proposed a numerical value for solubility as the square root of the cohesive energy density of a solvent, also known as a Hildebrand parameter. As the same van der Waals forces must be overcome whether a solvent is being vaporized or dissolved, the two must be related.

$$\delta = \sqrt{c} = \left[\frac{\Delta H - RT}{V_m} \right]^{1/2} \quad \text{Equation 1}$$

Where

δ is the Hildebrand parameter
 c is the cohesive energy density
 H is the heat of vaporization
 R is the gas constant
 T is the temperature
 V_m is the molar volume

Hildebrand postulated that for two solvents to dissolve in each other, their internal cohesive energies must be similar, and therefore solvents with similar Hildebrand parameters, must be soluble in each other as well(1).

In 1966, Charles M. Hansen related three independent parameters to the single Hildebrand parameter. The three Hansen parameters are dispersion force (d), polarity (p), and hydrogen bonding (h). Dispersion force was determined by matching the molecule to a similar alkane-structured molecule. Polarity was determined by measuring molecular dipole moments and comparing the functional groups of that molecule with that of the same functional groups in smaller molecules. Hydrogen bonding is the extent to which hydrogen bonding affects the overall polarity of the molecule. The relative contributions of these values were then calculated as fractions of the single Hildebrand parameter(1). Hildebrand parameters can be related to each of the three Hansen parameters in the following way:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad \text{Equation 2}$$

In theory, a solvent with all three Hansen parameters equal or almost equal to that of the Dioctyl Sebacate's parameters would be the perfect solvent and would greatly reduce the cleaning time of the metal(s) in question. Each of the three Hansen parameters are independent and can be graphed in three dimensional space.

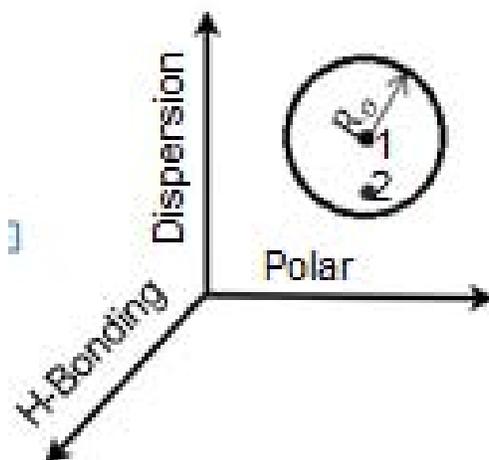


Figure 1. Hansen Parameters in 3-Dimensional Space.

R_o , in Figure 1, is the 3-dimensional radius in which the solvent in question can react. Therefore, all other reagents in that radius would be able to react with the solvent in question. R_A is another radial dimension that takes into account the separation between two chemicals in the three-dimensional space.

$$R_A = \sqrt{4 \cdot (\delta_{d,2} - \delta_{d,1})^2 + (\delta_{p,2} - \delta_{p,1})^2 + (\delta_{h,2} - \delta_{h,1})^2} \quad \text{Equation 3}$$

Equation 3, with subscripts 1 and 2 referring to solvent 1 and solvent 2 respectively, was developed by a colleague of Hansen and was found empirically (2).

The ratio R_A/R_o is known as the RED and it reflects the Relative Energy Difference. The closer the RED is to 0, the greater affinity the two solvents have for each other, the more soluble the two solvents are in each other. The further the RED is from 1, the lesser affinity the two solvents have for each other. (3)

For this study, solvents and detergents were chosen based on detergent/solvent availability, human hazard, and their ability to remove the soil of interest, Dioctyl Sebacate oil, based on predictions using Hansen solubility parameters. Solvents with similar Hildebrand solubility parameter values to that of the Dioctyl Sebacate oil were chosen for Hansen solubility comparison analysis.

A measurement of the remaining contamination on sample coupons was accomplished using nonvolatile residue (NVR) analysis. NVR measures the soluble material from an evaporated

effluent rinse of the sample. Ethanol was applied as the NVR rinse solvent for all samples in this study.

II. EXPERIMENTAL

Solvents Evaluated

Laboratory reagents, including materials qualified for program work, with similar Hildebrand values to the Dioctyl Sebacate were chosen and R_A -values were computed between each reagent and the Dioctyl Sebacate oil. Pairs with smaller R_A -values are predicted to be more miscible and the paired solvent cleaning more efficient.

The following is a predictor list from relative best to “worst” solvent for the Sebacate oil found by the computed R_A -values.

Table 1. Cleaning agent predictor list.

R_A	Cleaning Solvent/Detergent
1.4	1,1,1-Trichloroethane
3.1	Diethyl ether
3.5	N-methyl-2-pyrrolidone (NMP)
3.6	D-limonene
3.6	Amyl acetate
3.7	cyclohexane
4.0	hexane
6.1	Dimethyl sulfoxide (DMSO)
8.1	ethanol

Best ↑
↓ Worst

Based on the Hansen Parameters of solvents and the manufacturer’s recommendation, diethyl ether, NMP, D-limonene, hexane, and ethanol were chosen for testing. All chemicals used are reagent-grade or better. Synergy 3000 CCS™ (Synergy), a critical cleaning solvent blend of terpene and heterocyclic alcohol solvent developed at the Honeywell FM&T Kansas City Plant, and industrial-grade Brulin, a commercial detergent, were also chosen for testing. Synergy is a new laboratory reagent under consideration for program work and Brulin is currently used in the laboratory. Neither cleaners has listed Hansen parameters available for comparison.

Sample Preparation and Cleaning Procedure

1’’x1’’ stainless steel (304SS) coupons were coated in the Sebacate oil at ambient temperature. Each were dipped in the Sebacate oil and wiped clean with a dry, clean-room wiper.

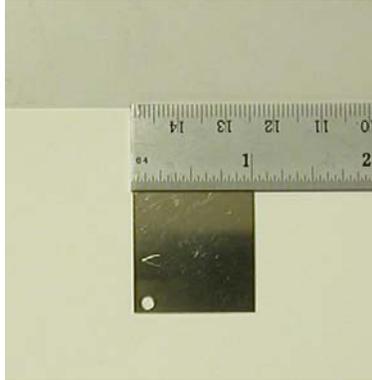


Figure 2. 304SS coupons used for testing.

In a class 1000 clean room, each cleaner was tested for non-volatile residue applying varying cleaning/soak times (5 and 10 minutes). Brulin was tested at two volume concentrations (5 and 15%) and both Brulin and NMP were tested at two different temperatures as well.

All glassware utilized for this experiment were ultrasonically cleaned in Brulin for 5 minutes, rinsed well with DI water ($\geq 15\text{M}\Omega\text{-cm}$), and ethanol-rinsed with a squirt bottle three times before being blown dry with nitrogen.

Table 2 lists the test matrix for the study.

Table 2. Test Matrix

Agent	Temperature (°C)	Concentration (vol%)	Time (min)	Coupon #	BP (°C)	Rinse Agent
diethyl ether	25 (ambient)	100	5	21	34.6	Ethanol
			10	22		
NMP	60		5	15	202-204	Water
			10	17		
			5	16		
			10	18		
d-Limonene	50		5	13	176/178	IPA
			10	14		
Hexane	25 (ambient)		5	19	69	IPA
Ethanol			10	20		
			5	10	78.37	
10			12			
Burlin	60	15	5	5	100	Ethanol
			10	7		
		5	5	1		
			10	3		
	80	15	5	6		
			10	8		
		5	5	2		
			10	4		
Synergy CCS	25 (ambient)	100	5	9	assume near IPA	IPA/Water
			10	11		

A single-test NVR analysis rinse was taken of a control sample, Sebacate oil-coated coupon to determine approximate amounts of initial oil coating. The result of 0.38 mg non-volatile residue was lower than desired. At least 0.5 mg was desired for each coupon in order to better distinguish cleaning efficacy. Using a micro-syringe, 1 μ L of oil was added to each coupon by placing it on one side of the coupon. Another NVR analysis was then performed on another Sebacate oil-coated control coupon and there was 2.71 mg of non-volatile residue on the coupon – allowing for more distinguishable results.

Most coupons were submerged in their respective cleaning agent in a clean 300/400 mL beaker on a stirring hot plate, whether temperature was ambient or elevated. A stir bar was spun at 200 rpm. As it is very volatile and hazardous, the coupons cleaned with diethyl ether were manually agitated in the reagent at ambient temperature under a fume hood for the allotted amount of time.

III. TEST RESULTS AND DISCUSSION

All cleaners performed well as predicted by their solubility parameters as indicated by the low NVR values. A single coupon was used for each cleaning method.

Table 3. Test Results
(Values are considered ± 0.05 mg)

Agent	Temperature (°C)	Concentration (vol%)	Time (min)	Coupon #	BP (°C)	Rinse Agent	NVR (mg)	
diethyl ether	25 (ambient)	100	5	21	34.6	Ethanol	0.00	
			10	22			0.00	
NMP	60		5	15	202-204	Water	0.02	
			10	17			0.01	
			5	16			0.00	
			10	18			0.00	
d-Limonene	50		5	13	176/178	IPA	0.02	
			10	14			0.01	
Hexane	25 (ambient)		5	19	69		0.01	
			10	20			0.00	
Ethanol			5	10	78.37	0.01		
			10	12		0.01		
Brulin	60		15	5	5	100	Ethanol	0.05
				10	7			0.06
		5	5	1	0.04			
			10	3	0.05			
	80	15	5	6	0.05			
			10	8	0.06			
		5	5	2	0.06			
			10	4	0.02			
Synergy CCS	25 (ambient)	100	5	9	assume near IPA	IPA/Water	0.04	
			10	11			0.00	

The data indicates that diethyl ether, heated NMP, hexane, and ethanol are the best of the cleaners tested as shown in Table 3. Because it is a hazardous material, diethyl ether is not suitable.

The labor required for each type of cleaning must be taken into account when evaluating results. The effort in heating a cleaning solution adds time and cost. Although NMP and diethyl ether cleaned well, other solvents performed equally well so NMP and diethyl ether were not chosen for use. Synergy may also be a good candidate, though more tests need to be undertaken to confirm a longer time period would be required. Ambient temperature NMP, d-Limonene, and Brulin are only fair candidates. Brulin-cleaning may be taken out of the cleaning regimen with negligible effect. The NVR results demonstrate better cleaning with solvents, indicating solvent use will require less time. The preparation and application of this cleaning method in addition to solvent cleaning extends the cleaning process time, further increasing the cost.

It should be noted that heating the transducer to approximately 50°C, the temperature previously verified for drying after cleaning, is likely to reduce cleaning time as heating the oil will make

the oil less viscous and easier to remove without adding risk to the part or process. Future experimentation would be required to evaluate this.

IV. REFERENCES

1. Kanegsberg, Barbara and Kanegsberg, Edward. *Handbook for Critical Cleaning Cleaning Agents and Systems*. Boca Raton, 2011. Print.
2. Kesters, E. *Selection of ESH solvents for cleaning applications in semiconductor manufacturing* [Powerpoint slides]. Retrieved from <http://www.mstconf.com/UMaine%20Presentations/Particle11-TBearda.pdf>
3. *Hansen Solubility Parameters: A User's Handbook*. Retrieved from [http://home.eng.iastate.edu/~mkessler/MatE454/By_Class_Date/\(8\)%207%22Feb%2013/Reading%20assignment%20-%20Chapter%201%20from%20Hansen%20Solubility%20Parameter%20HHandboo.pdf](http://home.eng.iastate.edu/~mkessler/MatE454/By_Class_Date/(8)%207%22Feb%2013/Reading%20assignment%20-%20Chapter%201%20from%20Hansen%20Solubility%20Parameter%20HHandboo.pdf)

DISTRIBUTION

1 MS0665 Mark Benner Org. 02541

1 MS0959 Deidre Hirschfeld Org. 01832

1 MS0899 Technical Library 9536 (electronic copy)

For LDRD reports, add:

1 MS0359 D. Chavez, LDRD Office 1911

For CRADA reports add:

1 MS0115 OFA/NFE Agreements 10012

For Patent Caution reports, add:

1 MS0161 Legal Technology Transfer Center 11500



Sandia National Laboratories