CRC Report No. AV-26-17

# DEVELOPMENT OF INDUSTRY REFERENCE FLUIDS FOR ASTM D3241 TESTING

# **Final Report**

December 2020



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UDR-TR-2020-81

# Development of Industry Reference Fluids for ASTM D3241 Testing

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December 2020

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# **EXECUTIVE SUMMARY**

Assurance of aviation turbine fuel thermal stability is a necessary check for today's modern aircraft. While many methods exist to examine jet fuel thermal stability, the only allowed method for assessing jet fuel thermal stability—for most internationally recognized jet fuel specifications—is ASTM D3241. A confluence of recent events, such as: introduction of metrological methods of heater tube rating, reported variations between D3241 instrument versions, and observed variability of D3241 results during the ASTM Interlaboratory Crosscheck Program, has given rise to a desire for a means of verifying the test equipment used for thermal stability evaluation. In an effort to improve thermal stability reference fluid. The candidate fluid contains organo-nitrogen and organo-sulfur species to closely replicate actual jet fuel thermal instability issues often encountered in commercial fuels.

It was found that the chemical formulation (both the choice of instigating chemical species and the concentration of the species), as well as the ASTM D3241 operating temperature strongly influence the magnitude and location of surface deposition on heater tube specimens and the magnitude of system pressure drop. Accelerated storage stability results indicate a candidate reference fluid could be shelf stable for at least 12 months. Preliminary interlaboratory (pre-ILS) results are provided for both a high depositing and low depositing fluid. The pre-ILS results indicate excellent agreement for pass/fail surface deposit results, however, absolute deposit values vary.

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# INTRODUCTION

Thermal stability of aviation turbine fuel—that is, the propensity of a fuel to produce nuisance carbonaceous deposits due to oxidative pathways at elevated temperatures is an important performance property. The long approved quality assurance/quality control (QA/QC) method for assessing the thermal stability of aviation turbine fuels has been ASTM D3241 (and the technically equivalent IP 323). It is known that the precision of D3241 deposition ratings, as evaluated using the visual rating method or VTR (Annex A1), have the highest uncertainty around the most common pass/fail specification point, i.e., less than 3 color code [ASTM International, 1993]. Additionally, recent results from an ASTM Crosscheck Study have shown that metrological methods of heater tube evaluation, i.e., ellipsometric tube rating (ETR, Annex A3) and interferometric tube rating (ITR, Annex A2), also show high uncertainty for a fuel at or near "failing" status [Bower, 2016; Bower, 2019]. That is to say that D3241 has the lowest uncertainty, i.e., highest confidence, for assessing fuels of very "high" and very "low" stability, but the opposite is true for assessing fuels that are of "marginal" stability where D3241 has high uncertainty, i.e., low confidence. While these observations may give industry participants pause about the interpretation of D3241 results, especially for marginal fuels, the longevity and pervasiveness of the method itself means it would be difficult to transition to a completely different method of thermal stability assessment. It is therefore important to assess the precision of not only current instrumentation and consumables, but also future iterations of the apparatus itself.

Observations of D3241 repeatability and reproducibility have always been made using real aviation turbine fuels, which are in either limited or finite quantity and so means they cannot be reproduced over long periods of time. Real commercial fuels tend to be poorly characterized with respect to their trace composition and the thermal stability performance of real fuels can change over time due to storage and handling conditions. Fuel trace composition is known to be a significant cause of thermal instability in fuels [Hazlett, 1991; Zabarnick et al., 2019], however, the exact chemical composition of poor fuels is variable and often difficult to monitor without highly sophisticated research analysis techniques [Kuprowicz et al., 2007]. There is no consistent thermal stability reference fluid that is both well characterized and reproducible over long periods of time. Therefore, it is difficult to identify specific instrumentation factors that might contribute to high method uncertainty.

With these concepts in mind, the Coordinating Research Council (CRC) initiated a program to develop one or more thermal stability reference fluid(s) for use with ASTM D3241 and/or IP 323. The initial program objectives were twofold: 1) develop a reference fluid that produces a consistent surface deposit on D3241 heater tube specimen, and 2) develop a reference fluid that produces a consistent fluid that produces a consistent produces a consistent D3241 heater tube specimen, and 2) develop a reference fluid that produces a consistent fluid that produces a consistent produces a consistent D3241 heater tube specimen, and 2) develop a reference fluid that produces a consistent D3241 heater tube specimen produces a consistent produces a consistent D3241 heater tube specimen produces a consistent produces a consistent D3241 heater tube specimen produces a consistent produces a consistent D3241 heater tube specimen produces a consistent produces a consistent D3241 heater tube specimen produces a consistent produces a consistent D3241 heater tube specimen produces a consistent produces a consistent D3241 heater tube specimen produces a consistent D3241 pressure produces prod

differential response. Both objectives were to be met using chemistry that proceeds via known thermal-oxidative pathways, in an effort to more closely represent fouling experienced by real fuel samples. It was originally specified that the D3241 testing should be conducted between 250 to 300°C (preferably at either 260 or 275°C) and that the pressure differential should reach 100 mmHg within 60 to 90 minutes of test duration under similar temperature conditions. A single fluid to achieve both tasks was desirable, however, multiple reference fluids could also be used. After starting the program and reporting of initial results, the CRC project panel (i.e., the industry panel overseeing this work) relaxed the pressure differential requirements, and emphasized the use of the preferred temperatures, i.e., 260 or 275°C, for the surface deposit reference fluid. However, based on recent thermal stability issues reported in the field, a reference fluid for differential pressure remains a valid interest. Additionally, it was never the intent of this project to produce a finished test fluid, but rather to provide a test fluid that would then be subjected to interlaboratory study (ILS) procedures before being added to ASTM D3241 or IP 323. We present our findings on the development of such reference fluids herein.

# **EXPERIMENTAL**

Reference fluid candidates were subjected to thermal stress according to the ASTM D3241 method using a single ALCOR Mark III JFTOT® apparatus. Heater tube specimen were generated using clean (new) standard aluminum Falex heater tubes (P/N: 400-560-001) in accord with ASTM D3241. The heater tube specimens were evaluated after testing using both a Falex Model 430 ellipsometer and an AD Systems DR10 interferometer according to D3241 Annex 3 and Annex 2, respectively. Table 1 lists the chemicals used as instability instigating compounds in this study. All chemicals were 98% pure (or greater) and were procured from Sigma-Aldrich; chemicals were used as received from the manufacturer. Table 2 lists the products used as base solvent; base solvents were used as received from the manufacturer unless otherwise specified. Mixtures of N and S compounds, in an aliphatic solvent, were hand prepared in small batches. All N and S compounds were readily dissolvable at ambient conditions with the exception of phenyl disulfide (PhS<sub>2</sub>Ph) which was a solid that required about 5 minutes of mixing in an ultrasonic bath to dissolve.

Compound Name (Abbreviation)	CAS No.	Chemical Formula	Molecular Weight	Phase (Ambient)
Hexylamine (HA)	111-26-2	$C_6H_{15}N$	101	Liquid
Dodecylamine (DDA)	124-22-1	$C_{12}H_{27}N$	185	Solid (waxy)
3,5-Dimethylaniline (DMA)	108-69-0	$C_8H_{11}N$	121	Liquid
n-Hexyl sulfide (HS)	6294-31-1	$C_{12}H_{26}S$	202	Liquid
Phenyl disulfide (Ph <sub>2</sub> S <sub>2</sub> )	882-33-7	$C_{12}H_{10}S_2$	218	Solid
2-Ethylphenol	90-00-6	$C_8H_{10}O$	122	Liquid

### Table 1. List of Instigating Compounds

### Table 2. List of Aliphatic Solvents

Product Name	Product Code	Manufacture
Exxsol™ D80 Fluid	n/a	ExxonMobil Chemical Co.
Exxsol™ D110 Fluid	n/a	ExxonMobil Chemical Co.
Deodorized 175 Solvent	VS-DEO175	Rock Valley Oil & Chemical
ShellSol™ D80	Q7722	Shell Chemical LP
LPA®-170 Solvent	n/a	Sasol Chemicals LLC

### Accelerated Storage Testing

Accelerated aging of selected solvents/samples at 43°C over a period of 12 weeks was performed in an effort to simulate long-term (i.e., 12 month) ambient storage. Candidate solvents were stored either with or without deposit instigating additives, and either in the presence or absence of oxygen (i.e., air). For solvent stored without N & S compounds, the instigating chemicals were added after storage, just prior to D3241 testing. Samples stored in the absence of oxygen were nitrogen sparged for about 15 minutes (at a gentle rate) to displace oxygen (dissolved and in the container ullage) prior to sealing the one gallon, epoxy lined metal container. No active gas sparging was performed on samples stored air saturated since it was assumed that normal handling of the samples (e.g., pouring/transferring between containers) provided sufficient air saturation. Samples were tested according to ASTM D3241 prior to aging and after both 6 and 12 weeks of accelerated aging. Control samples of each fluid were stored at ambient laboratory conditions throughout the 12-week period and were tested at coincident time intervals as the aged samples. Table 3 shows the number of replicate samples run for each test condition; data were collected on a total of 36 D3241 runs.

		Replicates					
Stored Sample	Hoodenaaa	Storage Duration (weeks)					
Stored Sample	пеаизрасе	0	6	12	6	12	
	-	Ambient			43°C		
Exxed D90	Air	1	1	1	3	3	
	Nitrogen	1	1	1	3	3	
Exxsol D80 + Ph <sub>2</sub> S <sub>2</sub> 200 mg/L +	Air	1	1	1	3	3	
HA 100 mg/L + DMA 100 mg/L	Nitrogen	1	1	1	3	3	

Table 3.	Accelerated Aging	Test Matrix,	Number of	<sup>f</sup> Replicate	Samples pe	er Storage
		Trea	atment			

# **RESULTS AND DISCUSSION**

Previous research has shown that combinations of S, N, and O containing heteroatomic species (dissolved in either fuel or solvent) can cause thermal-oxidative deposition at 140°C in a guartz crystal microbalance (QCM) apparatus (ASTM D7739) in a matter of hours [Zabarnick et al., 2017]. Additional studies have demonstrated that these S, N, and O heteroatomic species, in combination, can cause deposition using a D3241 apparatus, even though temperatures and residence times are considerably different in D3241 than those of D7739, e.g., fuel experiences non-isothermal conditions in D3241 with a maximum wetted wall temperature of typically 235–325°C and residence times of seconds [Zabarnick et al., 2019]. In addition to sulfur and nitrogen containing compounds, the original request for proposal from the CRC suggested other potential deposit instigating components for exploration such as: nitrate type Cetane improver, low molecular weight polyisobutylene succinimides (PIBSI) [Reid & Barker, 2013], zinc neodecanoate [Lacey et al., 2016], and 2-methylindole and/or copper [Taylor, 2002]. However, our decision to pursue S, N, and O as instigating compounds is due to our extensive research on real aviation turbine fuels [Kuprowicz et al., 2007; Zabarnick et al., 2016; Zabarnick et al., 2017; Zabarnick et al., 2019]. We believe these heteroatomic compounds are the frequent cause of thermal instabilities in jet fuel and thus represent realistic pathways to deposit during D3241 testing.

## **Preliminary Studies**

One challenge with this program is the very large parameter space that can be explored to achieve the desired outcome. Based on our past experiences, we chose to limit the number of organo-nitrogen and organo-sulfur containing compounds to a few each, while exploring other factors such as set point temperature (that is the maximum wetted wall temperature), species combinations, and instigating material concentration. Figure 1 shows some of the preliminary work investigating instigating species mixtures. This figure shows deposition profiles, i.e., circumferentially averaged ETR deposit thickness versus axial length along a heater tube specimen, for the neat solvent (Exxsol D80) and four different mixture combinations of possible instigating compounds. The neat solvent presents no measurable deposit, however, with the addition of appropriate N and S compounds significant levels of deposition are formed between about 35 to 55 mm along the tube. As reported elsewhere, the maximum heater tube wetted wall temperature occurs between about 30 to 40 mm with sharp declines in temperature as the heater tube entrance and exit points are approached [Sander et al., 2015]. The nature of the heater tube wall temperature is due to the cooled bus bars (near the entrance and exit) along with the resistive heating of the aluminum heater tube. The drastic rise in surface deposits seen on these tube specimens (Figure 1) appears connected to the maximum wetted wall temperature. Additionally, dissolved oxygen

concentrations, both before and after the heater tube section, were monitored for some of the initial candidate reference fluids using an InPro 6850i polarogaphic oxygen sensor (Mettler-Toledo, LLC, Columbus, OH). The resulting changes in the dissolved oxygen showed *complete oxygen consumption* for the cases measured (data not shown), thus the measurements were discontinued for subsequent trials. These observations combined, i.e., oxygen consumption and temperature sensitivity, demonstrate that the observed surface and bulk deposition products are due to known thermal-oxidative chemical pathways.



Figure 1. D3241 heater tube profiles, via ETR, of average circumferential deposit thickness with various mixtures of N and S compounds in Exxsol D80 at either 275 or 280°C; all N and S compounds added at 200 mg/L each (nominal).

Having established that deposits could be produced using an aliphatic solvent with a few compounds added at low levels, a study was conducted to vary the concentration of the instigating compounds for the following two mixture blends: 1) HA + Ph<sub>2</sub>S<sub>2</sub>, and 2) DMA + HS. The resulting D3241 data, taken with a set point temperature of 300°C, are listed in Table 4. As the table shows, the deposit max spot thickness increases as concentration increases for both mixture sets. And while the DMA + HS mixture shows no  $\Delta P$  at either concentration, the HA + Ph<sub>2</sub>S<sub>2</sub> mixture gives a moderate amount of  $\Delta P$ , 6.5 mmHg, at the lower concentration and a maximum amount of  $\Delta P$ , 280 mmHg, at the higher concentration tested. These results demonstrate that the choice of instigating compounds in the mixture influence both the surface deposition and pressure drop

magnitude. Additionally, the concentration of a given mixture seems to influence deposition in a proportional manner.

Specie	es Conce	ETR Max	Max ∆P		
HA	DMA	$Ph_2S_2$	HS	Spot (nm)	(mmHg)
100	-	100	-	107	6.5
200	-	200	-	157	280
-	200	-	200	40	0
-	300	-	300	77	0

Tahle 4 D3241 Results	for Mixtures o	f Exysol D80 and	Various Com	nounds at 300	)9
TUDIE 4. DOZAT NESUILS	jui iviiktuies u	LXXSUI DOU UIIU	vurious com	pounus at 500	/ C

It is clear that low levels of organo-nitrogen and organo-sulfur containing compounds can be combined to produce both surface deposits and pressure drop in D3241 studies, with the amounts and profiles of products being concentration and mixture specific. It was also of interest to explore what effect set point temperature had on the method results. Figure 2 shows replicate runs of a mixture of Exxsol D80 with HA 200 mg/L and  $Ph_2S_2$  200 mg/L as a function of temperature. As this figure shows, the onset of deposition within the tube shifts further upstream as the set point temperature increases. This makes intuitive sense as reaction rates accelerate significantly with temperature thus forcing oxidation and deposition reactions to occur earlier within the heated portion of the tube. Similarly, Figure 3 shows pressure drop profiles for the same set of replicate runs with respect to temperature. As these data show, the 300°C runs produce a maximum level of  $\Delta P$ , 280 mmHg, between about 90 to 100 minutes within the run, thereby initiating the filter by-pass. This level, and rate, of pressure drop satisfies the original  $\Delta P$  target (shown on Figure 3 with red box); however, this target  $\Delta P$ could not be attained at lower operating temperatures. Significantly less pressure drop is exhibited at 275°C and even less still at 260°C. These data indicate that meeting the originally prescribed differential pressure objective is possible when operating at 300°C with 200 mg/L each of HA and  $Ph_2S_2$ .

Table 5 lists the max spot thickness and max pressure drop for each of the replicates shown in Figure 2 and Figure 3 along with average values. As these data show, higher variability was observed for both surface deposits and  $\Delta P$  values from the 275°C set point experiments opposed to the 260 and 300°C runs. It is possible that deposits produced at 275°C caused ETR detector saturation (around 180 to 220 nm), thus increasing variability in the data. It stands to reason that at 300°C the temperature is sufficiently great to force the chemistry to take place—to completion—in a narrow window of time and space along the heater tube, thus providing repeatable deposition profiles (see Figure 2). A similar explanation applies to bulk insoluble product formation at the higher temperature for the chemistry used in these experiments, therefore leading to repeatable  $\Delta P$  observations at 300°C. In contrast, experiments conducted at 260°C might be sufficiently low in temperature for the chemical kinetic rates to produce an incipient—or near incipient—level of deposit within the allowed residence time of the D3241 apparatus. This is demonstrated by examination of the deposition profiles in Figure 2, whereby deposits are forming very near the end of the heater tube. As is the case for all of the temperature runs shown, the onset of deposit appears to be relatively consistent with this chemistry.



Figure 2. Profiles of average circumferential deposit along D3241 heater tubes with respect to set point temperature for mixtures of Exsol D80 with HA 200 mg/L and Ph<sub>2</sub>S<sub>2</sub> 200 mg/L; orange/brown-circle markers are at 300°C (n=3), blue-triangle markers are at 275 °C (n=5), and grey/black-square markers are at 260 °C (n=3).

Ph2S2 200 mg/L							
T (°C)	ETF	R Max (nm) p	Avg	Std			
	1	2	3	4	5	-	Dev
260	141	144	132			139	7
275	154	150	208	216	153	176	33
300	157	160	161			159	2
	Max	Pressu	ure Dro	op (mn	nHg)		
T (°C)		per	Replic	ate	0.	Avg	Std
	1	2	3	4	5	-	Dev
260	1	3	3			2	1
275	68	14	39	34	17	34	22
300	280	280	280			280	0

Table 5. Maximum D3241 Values for a Mixture of Exxsol D80 with HA 200 mg/L and



Figure 3. Temporal profiles of pressure drop for D3241 runs using mixtures of Exxsol D80 with HA 200 mg/L and Ph2S2 200 mg/L; 300  $^{\circ}$  runs tripped instrument bypass around 90 to 100 min; originally requested CRC target  $\Delta P$  zone shown as red box.

Numerous trials were performed, with various combinations of nitrogen and sulfur containing compounds, in an effort to identify a reference fluid that satisfied the suggested requirements, i.e., significant level of surface deposition and significant level of pressure drop. After seeing the initial reported data, the CRC project panel recommended that a set point temperature of either 260 or 275°C would be the most desirable since most D3241 operators are comfortable with these settings. Therefore, the higher temperature runs were abandoned and focus was shifted to 275°C. This temperature restriction prohibited attaining the originally desired  $\Delta P$  objective. However, some promising mixture results were obtained at 275°C and are listed in Table 6. From these seven mixtures, two mixtures were selected for further inspection (shaded in red and blue) based on the repeatable deposition results and the ability to provide a  $\Delta P \ge 1$  mmHg in the same run. Figure 4 shows replicate deposit profiles from these two down-selected mixtures. As this figure shows, the mixture containing a combination of  $Ph_2S_2 + HA + DDA$  (Fig. 4a, and shaded in red in Table 6) gives a more gradual deposition profile with the maximum deposition occurring near the end of the measured portion of the heater tube. The mixture containing a combination of  $Ph_2S_2 +$ HA + DMA (Fig. 4b, and shaded in blue in Table 6) produces a more abrupt rise in deposits just past half way down the heater tube. Based on these profiles, the latter

combination (shown in Fig. 4b) appears to be more favorable as a reference fluid and thus was advanced as the primary candidate fluid for additional robustness testing.



Figure 4. D3241 heater tube profiles at 275  $^{\circ}$ C of Exxsol D80 with a) Ph<sub>2</sub>S<sub>2</sub> 150 mg/L + HA 50 mg/L + DDA 100 mg/L or b) Ph<sub>2</sub>S<sub>2</sub> 150 mg/L + HA 100 mg/L + DMA 100 mg/L.

Nominal Concentrations (mg/L)			ETR Max Spot Thickness (nm)			Max DP (mmHg)			
$Ph_2S_2$	HA	DDA	DMA	Value	Avg	σ	Value	Avg	σ
				122			0.6		
				103			1.8		
	100	-	-	124	132	23	0.5	0.8	0.5
100				153			0.7		
				158			0.6		
	-	100	-	41	42	2	-	0.0	n/a
				44			-		
	150			191	191	0	3.9	41	53
				191			7 1		
150				1.07			7.1 5.2		
150	50	100	_	141	131	Q	0.Z	11	11
	50	100	-	122	151	3	70		
				125			7.9 15		
				154			68.0		
				150			14.4		
				208			38.6		
	200	-	_	216	173	27	33.9	33	18
	200			153			17.0	00	
				174			37.1		
				159			20.4		
				90			0.3		
200	-	200	-	93	83	15	0.3	0.2	0.2
				66			-	•	•
				145			33.8		
				159			13.7		
	400		100	134		4.0	23.3		
	100	100 -		152	150	10	105.5	31	38
				161			1.5		
				153			8.2		

Table 6. Deposit Thickness and Max Pressure Drop Results for Select Samples at 275°Cvia D3241 (Shaded Rows Are Recommended Formulations)

Note: mixture shaded in blue is referred to as "Fluid A" later in this report.

### Fluid Parameter Studies

Assessment of the "ruggedness and sensitivity" of parameters that might impact reference fluid results will now be addressed. The critical parameters of material/chemical sourcing and storage/handling are outlined in the following subsections.

### Chemical Selection/Sourcing

The base solvent used for the majority of this work is a dearomatized, hydrocarbon distillate within the jet fuel distillation range, i.e., Exxsol D80. A selection of other comparable solvents that were tested are listed in Table 2. All five solvents are reported to be "deodorized" or "dearomatized," i.e., aliphatic, distillate fractions of a similar flash point (with the exception of Exxsol D110 which has a slightly higher flash point). These solvents were tested via ASTM D3241 at 275°C both with and without the deposit promoting additive mixture: HA 100 mg/L, DMA 100 mg/L, and Ph<sub>2</sub>S<sub>2</sub> 200 mg/L (this mixture, in Exxsol D80, is referred to as "Fluid A" later in this report). The resulting heater tube deposition profiles are shown in Figure 5. These results show minimal to no deposit from all the neat solvents tested (note: neat LPA-170 solvent was not tested due to material availability). These data also show that the additive mixture promoted significant deposition in all cases. The general form of these deposition profiles are solvent, indicating minimal impact due solely to the solvent manufacture/product. Rather—and more beneficially—the addition of the instigating N & S materials appears to be the primary source of surface deposits.



Figure 5. Heater tube profiles of solvents with and without deposition additive mixture (phenyl disulfide 200 mg/L, hexylamine 100 mg/L, 3,5-dimethylamine 100 mg/L) at 275°C; fuel flow in tube from left to right.

Outside of vendor differences with solvent, we explored the use of clay to pre-treat various solvents before adding the deposit instigating mixture. Figure 6 shows the results of this experiment. As the data show, pre-treatment of the various solvents using clay decreases the absolute amount of surface deposits formed for all three solvents examined. The cause for this is not yet conclusive. We speculate that the clay is removing some trace compound(s) found in each of the solvents examined, such as hydroperoxides; however, an exhaustive study of this nature is outside of the current scope of this project. Regardless, the three solvents appear to give consistent results relative to each other when all are pre-treated with clay or used as is from the manufacture.



Figure 6. Heater tube profiles of solvents both with and without clay treatment; all samples contain phenyl disulfide 200 mg/L, hexylamine 100 mg/L, 3,5-dimethylamine 100 mg/L and were stressed at 275 °C.

Differences in raw material age were examined by using both "old" and "new" instigating chemicals to test the shelf stability of these pure chemicals. All chemicals were used as is from the manufacture; "older" materials had been stored in ambient, laboratory conditions (approximately 70°F, in dark cabinets) for up to nine years, while "new" materials were all procured within 9 months of use (use date was 27-Apr-2019). Received dates for older materials were as follows: phenyl disulfide = Oct 2000, hexylamine = Dec 2016, and 3,5-dimethylaniline = Jan 2004. Figure 4 shows results of this experiment. Good repeatability is demonstrated for single runs. This gives confidence in the shelf stability of the pure instigating materials under reasonable conditions.



Figure 7. Heater tube profiles using "old" and "new" lots of heteroatomic materials; all samples contain phenyl disulfide 200 mg/L, hexylamine 100 mg/L, 3,5-dimethylamine 100 mg/L and were stressed at 275 °C.

Accelerated Aging Study

Additional "ruggedness" testing involved the accelerated aging of solvents at 43°C over a period of 12 weeks. Candidate solvents were stored both with and without deposit instigating additives, and in the presence and absence of oxygen. For solvent stored without N & S chemicals, the instigating mixture was added after storage, just prior to D3241 testing. Samples stored in the absence of oxygen were nitrogen sparged for about 15 minutes (at a gentle rate) prior to sealing the one-gallon container. Table 3 shows the number of replicate samples run for each test condition; data were collected on a total of 36 runs. The three ambient temperature replicates, for each sample and headspace condition, were run over the course of 12 weeks, while the accelerated aging samples were run in triplicate shortly upon completion of being aged. Average deposit profiles (with error bars depicting one standard deviation) for these data are shown in Figure 8 through Figure 10.

Figure 8 shows average deposition profiles for the four different sample preparations in the accelerated aging study stored at ambient temperature (control samples). Ultimately, each sample contains the same concentration of instigating compounds upon test, i.e., Exxsol D80 with  $Ph_2S_2$  200 mg/L, HA 100 mg/L, and DMA 100 mg/L, and the difference is in when the instigating compounds are added and whether or not the mixture is stored in the presence of oxygen. As these data show, there is excellent agreement in deposition profiles regardless of sample preparation treatment, and

relatively low variance within the data over the course of 12 weeks. These results are not surprising considering the prior data collected on this mixture and maintains confidence in our ability to replicate results under well controlled conditions over time.



Figure 8. Average deposit profiles (conducted over a 12-week period) of reference Fluid A (see Table 6) stored at ambient temperature; error bars show one standard deviation with n=3.

Figure 9 shows average (n=3) deposit profiles of samples after 12 weeks of accelerated storage at 43°C. These elevated temperature conditions are designed to simulate storage over the course of approximately 12 months under typical ambient conditions. These data show that deposition profiles are qualitatively similar regardless of the sample treatment, and that deposit values are within the given uncertainty of the test.

Finally, Figure 10 shows the progression of a single sample treatment, i.e., stored with instigating compounds in the presence of air, over the full 12 week period. This treatment is considered to be the most severe as the instigating materials could be susceptible to oxidation reactions during storage that could change the response of the compounds when tested using D3241. However, like the results shown in Figure 8 and Figure 9, the data shown in Figure 10 demonstrate there is excellent agreement of deposition profiles over the full 12 weeks of aging. These data increase our confidence that the candidate reference fluid, with instigating material, is reasonably "shelf stable." That is to say, we observe no evidence of degradation in performance, even under accelerated storage conditions.



Figure 9. Average deposit profiles of reference Fluid A (see Table 6) after 12 weeks of storage at 43°C; error bars show one standard deviation.



Figure 10. Average deposit profiles of reference Fluid A (see Table 6) samples after 0, 6, and 12 weeks of accelerated storage at 43°C.

### **Repeatability Assessment**

The previous section demonstrates that the sample treatment, e.g., storage condition, seems to be an insignificant factor on the resulting deposition profile of candidate reference Fluid A. Therefore, if we consider all 36 of these runs as replicates we can start to develop a more robust assessment of variability and uncertainty for this test fluid (on a single instrument). Table 7 lists average values, standard deviations, and ranges for both the max spot thickness and pressure difference measurements for these replicate runs, while Figure 11 shows histograms of the same data set to aid with visualization of the recorded value distribution. These data indicate a relative standard deviation of about 14% for max spot thickness and about 91% for the pressure difference. Although the pressure difference data values give significant variability, most values measure between about 2 to 17 mmHg. That is, in every case a pressure drop of at least 2 mmHg was recorded.



Table 7. Results of n=36 Observations for Exxsol D80 with Ph<sub>2</sub>S<sub>2</sub> 200 mg/L, HA 100 mg/L, and DMA 100 mg/L at 275  $^{\circ}$ C

Figure 11. Histograms of max deposit thickness and pressure difference measured for n=36 observations of Exxsol D80 with  $Ph_2S_2$  200 mg/L, HA 100 mg/L, and DMA 100 mg/L at 275 °C.

### Reproducibility Assessment

A preliminary interlaboratory (pre-ILS) study was conducted to assess the reproducibility of the candidate fluid(s). Nine laboratories, in addition to our own laboratory, agreed to participate and provide anonymized data. The instructions sent to participant laboratories can be found in Appendix A. Based on feedback from the CRC project panel, and the broader fuels community partners, it seemed desirable to further formulate a reference fluid that produced a measurable amount of deposit, but was still of 'passing' level, i.e., having a max spot thickness between about 30 to 85 nm. Therefore, UDRI distributed two separate reference fluids to the various laboratories (see Table 8 for fluid formulations); Fluid A is the same formulation reported in the preceding Fluid Parameter Studies and Repeatability Assessment sections and is highlighted in blue in Table 6 (representing a high concentration and corresponding high depositing fluid), while Fluid B contains the same instigating compounds as Fluid A but in lower concentrations (with corresponding lower deposition). Fluid A and Fluid B were both generated gravimetrically in single batch quantities of 36.8 kg and 29.6 kg, respectively; concentrations reported in Table 8 were calculated based on a solvent density of 0.8006 kg/L and took into account compound purity. The Ph<sub>2</sub>S<sub>2</sub>, HA, and DMA were weighed and dissolved in a small (ca. 100 mL) amount of Exxsol D80 prior to combining in a clean, epoxy-lined drum; solvent was metered to the total mass, then the entire drum was vigorously blended. Aliquots of each batch were metered into commercially available UN rated, aluminum sample containers approved for jet fuel transportation; volumes shipped to individual laboratories varied based on the number of tests each participant agreed to perform.

	Durity	Measured	PPM	Concentration
FIUID A	Purity	Mass (g)	(mg/kg)	(mg/L)
$Ph_2S_2$	99%	9.2930	250.	200.
HA	99%	4.6467	125.	100.
DMA	98%	4.6936	125.	100.
Total Ma	SS <sup>a</sup>	36,800		
	Durita	Measured	PPM	Concentration
Fluid B	Purity	Measured Mass (g)	PPM (mg/kg)	Concentration (mg/L)
Fluid B Ph <sub>2</sub> S <sub>2</sub>	Purity 99%	Measured Mass (g) 7.4756	PPM (mg/kg) 250.	Concentration (mg/L) 200.
Fluid B Ph <sub>2</sub> S <sub>2</sub> HA	<b>Purity</b> 99% 99%	Measured Mass (g) 7.4756 0.7477	PPM (mg/kg) 250. 25.0	Concentration (mg/L) 200. 20.0
Fluid B Ph <sub>2</sub> S <sub>2</sub> HA DMA	<b>Purity</b> 99% 99% 98%	Measured Mass (g) 7.4756 0.7477 0.7561	PPM (mg/kg) 250. 25.0 25.0	Concentration (mg/L) 200. 20.0 20.0

Table 8. Single Batch Reference Fluid	l Formulations Used for Distributior
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<sup>a</sup>Total mass includes mass of instigating compounds and Exxsol D80 solvent.

A variety of test equipment was used during this phase of the study. Variables included both D3241 test apparatus (manufacturer and model) as well as heater tube manufacturer; the number of test setups for each combination of variables is listed in Table 9. Participating laboratories were asked to perform testing in triplicate for each test setup they offered to conduct; therefore, a total of 63 heater tubes were generated using test Fluid A and 44 heater tubes were generated using Fluid B. Two of the Fluid A experiments were conducted at 260°C rather than 275°C, which provided interesting data points for comparison, however, those two samples will be treated as outliers and will not be reported with the aggregate data set (therefore reducing the total number of Fluid A heater tube samples to 61). Another complicating factor with this study is the reliance upon the participant's method for heater tube rating. All laboratories rated tubes visually (VTR), but use of metrology methods varied. Since we requested heater tube specimens be return shipped to UDRI, we were able to rate the heater tubes using our own ETR and/or ITR device. When a laboratory reported responses for ITR, ETR, and multi-wavelength ellipsometric tube rating (MWETR) they were always used/reported. However, in cases when a laboratory was unable to report ETR or ITR data, UDRI tube ratings were reported to supplement the data accordingly (these supplemental data are reported in red typeset in Table 12 and Table 13).

		Fluid A		Fluid	В
	Tube Mnfr:	Falex	Alcor	Falex	Alcor
Instrument Mnfr					
Alcor Mark II		1	0	0	0
Alcor Mark III		4	4	3	3
Alcor Mark IV		3	4	2	3
Falex 400		2	2	2	1

# Table 9. Number of Test Setups Based on Fluid Type,Tube Manufacture, and Instrument Manufacture

Table 12 and Table 13 list the complete set of data collected from the reporting laboratories for reference Fluids A and B, respectively (Laboratory number zero is UDRI, all other laboratory identities have been blinded for reporting purposes). There are a few striking observations from these data: 1) all but five of the 61 heater tubes generated at 275°C using Fluid A (Table 12) produce a failing rating from all reported methods (VTR, ITR, ETR, and MWETR), and those five heater tubes only pass using the ITR (they fail via VTR and ETR); 2) all 44 heater tubes generated at 275°C using Fluid B (Table 13) produce a passing rating from at least one evaluation technique. That is to say that Fluid A produces a consistent heater tube failing result and Fluid B produces a consistent passing heater tube result across all laboratories and all apparatus types; Figure 12 through Figure 15 emphasize and characterize these points in more detail.

Figure 12 shows a box and whisker chart of metrology results for Fluid A heater tubes. Quartile calculations were performed using an exclusive median, and the mean value is shown on the chart as an 'X'. Ranges of the reported maximum spot thickness, with respect to analytical technique, are variable for the Fluid A results (Figure 12 and Table 10). Some of this variance is due to the fact that 42 (out of 61) of the heater tubes were given a non-numeric rating value of >85 nm via the ITR; and therefore, higher thickness deposits were excluded in the numeric ranges (thus skewing the distribution to lower values for the ITR). Similarly, we have experienced detector saturation with the ETR between about 180 to 220 nm; therefore, thick deposits (≥220 nm) become under reported and can again skew the average value. Results for the MWETR assessment gave both the highest average value, but also the greatest range of values. It is unclear from these data which metrology method produces the most accurate result, nevertheless, rating values for Fluid A were consistently well above the typical failure value of 85 nm regardless of rating technique used.



Figure 12. Box and whisker plot of results for Fluid A; 42 tubes produced an ITR value of >85 nm which are excluded from the plot data.

10510 10. 5101	isticul B											
	VTR	ח ד	Maximum Thickness	Spot s (nm)	∆P (mmHa)							
		ITR	ETR	MWETR	(mm¤g)							
Mean	4.0	115	178	283	18.9							
σ	0.4	46	34	101	55							
Maximum	4.5	218	244	474	280							
Minimum	3	60	104	151	0.7							
Observations (n)	61	19	61	12	61							

In a similar fashion, Figure 13 and Table 11 show metrology results for Fluid B. What is immediately apparent from these data is how similar the rating results are using ETR, ITR, and even the MWETR (note the small sample population) when the max spot thickness is less than 85 nm. The mean max spot thickness values, and standard deviations, for Fluid B listed in Table 11 show equivalency of the aggregated values among the three metrology methods with the average max spot value being reported between about 50 to 60 nm.



Figure 13. Box and whisker plot of results for Fluid B; one heater tube produced an ITR value of >85 nm which is excluded from the plot data.

	VTR	Maximum Spot Thickness (nm) △P				
		ITR	ETR	MWETR	(IIIIIII)	
Mean	1.6	50	60	61	6	
σ	0.7	17	29	7	38	
Maximum	3	79	187	73	250.1	
Minimum	0.5	18.2	30	54	0.0	
Observations (n)	44	43	44	6	44	

Table 11. Statistical D3241 Results at 275 ℃ of Fluid B

The agreement demonstrated by the heater tube mean values from multiple metrology methods should not overshadow the overall range of values recorded for the individual samples in this study. In fact, an attempt to capture potential factors involved in test variability, e.g., heater tube manufacture, instrument make/model, reference fluid deposit level, and laboratory, was built into the pre-ILS sample matrix. While it is outside

the scope of this project to analyze these data (see Table 12 and Table 13) in terms of characterizing the variability of D3241 itself, we submit that future efforts could use the data contained in this report to investigate the influence of these potential sources of variability. Instead, Figure 14 and Figure 15 show parity plots of numeric heater tube ratings for ETR versus ITR and ETR versus VTR, respectively, to demonstrate the breadth of values recorded. In theory, all of the data should collapse onto two points, i.e., singular values for Fluid A and Fluid B. In both Figure 14 and Figure 15, tubes that were rated as abnormal (A) or peacock (P) are highlighted in green. Again, since 42 heater tubes for Fluid A were rated as >85 nm using the ITR these values could not be plotted. While these two figures both demonstrate the positive correlation between rating techniques, the primary observation we are highlighting is the overall range of values for each identical batch of sample fluid. While the overwhelming majority of heater tube samples conform to Fluid A = Fail and Fluid B = Pass—independent of the rating method—the actual values recorded span a significant range of thicknesses. The cause of the large range in thicknesses (for both Fluid A and Fluid B) is believed to be due to both instrument/test specific factors and the stochastic nature of thermal stability deposition processes.



Figure 14. Parity plot of metrology rating results for heater tubes with numeric values; single abnormal (A) tube rating—with numeric results—highlighted in green.



Figure 15. Numeric heater tube results via ETR versus VTR codes for both Fluids A and B; A and P visual ratings—with numeric results—highlighted in green, "<" and ">" codes recorded as –/+ 0.5.

While surface deposition of D3241 tests was given as a primary concern, evaluation of pressure drop was a secondary item of interest for the candidate reference fluid(s). Figure 16 shows histograms of  $\Delta P$  values (listed in Table 12 and Table 13) for Fluid A and Fluid B. Fluid A provides a pressure drop of >1 mmHg for all but one run and five runs gave  $\Delta P$  values >25 mmHg. Fluid B produces significantly less pressure drop with the overwhelming majority of samples giving less than 1 mmHg  $\Delta P$  (the reason for the Fluid B outlier of 250.1 mmHg remains unknown). Based on these observations, if higher  $\Delta P$  values are desired then it is recommended that higher temperatures or alternative formulations be further explored (see for example Figure 3 and Table 5).



Figure 16. Histogram of pressure difference,  $\Delta P$ , measurements for: a) Fluid A, and b) Fluid B for ASTM D3241 runs at 275 °C (data tabulated in Table 12 and Table 13).

l ah	D2244	Tuba	Den	Heater		Max Sp	ot Thick	ness² (nm)	
Lab No.	Model	Mnfr	кер. No.	Tube S/N	Code <sup>1</sup>	ITR	ETR	MWETR	۵۲ (mmHg)
			1	SIFIX148	4.5	>85	208	-	5.5
0	220 MF III	Foloy	2	SIFIX051	4	>85	197	-	10.1
0	230 IVIK III	ralex	3	SIBIX387	4	>85	190	-	9.0
_			4	SIFIX133	3.5	>85	216	-	21.1
			1	TAKIX293	3.5	>85	131	-	5.3
	230 Mk III	Falex	2	TAKIX292	3.5	87	116	-	4.6
			3	TAJIX258	3.5	60	142	-	5.0
			1	20A02188	3.5	79	104	-	1.9
1	230 Mk IV	Alcor	2	20A02204	3.5	64	151	-	1.9
			3	20A02165	3.5	76	107	-	1.9
			1	SLUIX976	4	>85	155	-	4.0
	F400	Falex	2	SLUIX192	3.5	64	121	-	4.3
			3	SLUIX407	3.5	85	117	-	2.6
			1	18B40762	4	>85	216	-	3.7
	230 Mk III <sup>3</sup>	Alcor	2	19F23837	4	>85	213	-	5.8
2			3	19F23855	4	>85	210	-	3.1
Z			1	19F24150	4	>85	213	-	3.3
	230 Mk III <sup>3</sup>	Alcor	2	19F24183	4	>85	212	-	3
			3	19F24180	4	>85	219	-	6.6
			1	19G38323	4	105	181	222	8.2
	230 Mk III	Alcor	2	19G38245	3.5	87	127	196	2.5
2†			3	19G38274	ЗA	89	146	151	3.1
3'			1	GENEU076	ЗA	>85	189	349	1.3
	230 Mk III	Falex	2	GENEU028	3	103	195	474	1.5
			3	GELEU214	3.5	218	207	276	2.4
			1	19 60711	4	160	178	-	195.8
	220 MIL 11/3	Alcor	2	19 60682	4	158	188	-	24.6
	230 IVIK IV°	AICOI	3	19 60677	4	184	228	-	7.1
4			4	19J74473	4	112	172	-	6.6
			1	19 60679	4	144	209	-	9.1
	230 Mk IV <sup>3</sup>	Alcor	2	19160694	4	159	210	-	6.4
			3	19160674	4	152	217	-	7.4

# Table 12. Results from Preliminary Interlaboratory Study for FLUID AUsing D3241 with 275 ℃ Operating Temperature

	<b>D0044</b>	<b>T</b> . I .	<b>D</b>	Heater	VTD	Max Sp	ot Thick	ness² (nm)	
Lab No.	D3241 Model	l ube Mnfr	Rep. No.	Tube S/N	Code <sup>1</sup>	ITR	ETR	MWETR	۵۲ (mmHg)
			1	18B35629	4.5	>85	190	226	43.8
	230 Mk III	Alcor	2	18B35833	4.5	>85	172	214	2.5
Б			3	18B35845	4.5	>85	149	206	2.5
5			1	18B35837	4.5	>85	196	435	7.8
	230 Mk IV	Alcor	2	18B35851	4.5	>85	182	286	5.3
			3	18B35820	4.5	>85	183	358	2.5
			1	SGLIX037	4.5	>85	185	-	3
	230	Falex	2	SGLIX842	4.5	>85	180	-	2
			3	SKLIX797	4.5A	>85	161	-	2
			1	18E08547	4.5	>85	189	-	4.5
6	230 Mk III	Alcor	2	18E08486	4.5	>85	200	-	4.6
			3	18E08518	4A	>85	171	-	5.9
			1	18E08492	4.5P	>85	209	-	8.9
	F400	Alcor	2	18E08504	4.5A,P	>85	184	-	8.7
			3	18E08476	4A	>85	120	-	5.4
7††	230 MK IV	Alcor	1	19A38214	3	90	80	-	0.2
	230 IVIK I V	AICOI	2	19A38232	3	89	88	-	0.1
			1	TDXJY840	4A	>85	175	-	280.0
			2	TEIJY073	4A	>85	199	-	53.3
	230 Mk III	Falex	3	TDRJY212	4A	>85	216	-	16.2
o			4	TDIJY694	4A	>85	244	-	3.4
0			5	TGQJY646	4A	>85	152	-	280.0
			1	TEJJY900	4A	>85	191	-	4.6
	F400	Falex	2	TEHJY207	4A	>85	189	-	5.2
			3	TEJJY525	4A	>85	206	-	3.8
			1	SFRIX786	4.5	>85	173	-	2.7
	230 Mk IV	Falex	2	MLQBI816	3.5	>85	159	-	12
٥			3	MLJBI778	4A	>85	185	-	0.7
9			1	19 62763	4	>85	143	-	1.5
	F400	Alcor	2	19 62751	4	>85	147	-	2.1
			3	19 62744	3.5	>85	123	-	2.3

### Table 12. Results from Preliminary Interlaboratory Study for FLUID A Using D3241 with 275 °C Operating Temperature (Cont.)

<sup>1</sup>VTR codes of "<" or ">" are reported as -/+ 0.5 color unit.

<sup>2</sup> Metrology values reported in red were measured at UDRI.

<sup>3</sup> Participant laboratory ran tests with the same model of D3241 apparatus, however, unique serial number units were used for each set of replicates.

<sup>†</sup> Participant laboratory ran duplicate ITR, ETR, and MWETR readings, the median value from the two readings is reported.

<sup>††</sup> 260°C operating condition used to generate data; values included in table for informational purposes only (data is excluded from aggregate data analysis).

Lab	D3241	Tube	Rep.	Heater	VTR	Max S	pot Thick	ness² (nm)	ΔP
No.	Model	Mnfr	No.	Tube S/N	Code <sup>1</sup>	ITR	ETR	MWETR	(mmHg)
			1	SIFIX207	1.5	45	58		0.8
0	220 MI/ III	Foloy	2	SIBIX562	1	42	54		3.4
0	230 IVIK III	Falex	3	SIBIX377	1	40	53		1.5
			4	SIAIX397	1	52	74		1.4
			1	SLUIX227	2.5	34	36		0.6
	230 Mk III	Falex	2	SLUIX693	2.5	31	30		0.3
			3	SLUIX136	2	21	32		0.2
			1	20A02287	1.5	37	45		0.0
1	230 Mk IV	Alcor	2	20A02292	1.5	36	35		0.6
			3	20A02314	1.5	34	31		0.0
			1	SLUIX460	2.5	40	67		0.7
	F400	Falex	2	SLUIX691	3	68	63		0.5
			3	SLUIX619	2	18	41		0.8
			1	19F23847	1	36	33		0
	230 Mk III <sup>3</sup>	Alcor	2	19F23861	1	39	42		0
2			3	19F23849	0.5	41	47		0
2			1	19F24186	1	45	50		0
	230 Mk III <sup>3</sup>	Alcor	2	19F24221	0.5	62	58		0
			3	19F24192	0.5	71	52		0
			1	19G38246	1	38	43	54	0
	230 Mk III	Alcor	2	19G38269	1.5	38	52	57	0
34			3	19G38342	1	57	71	65	0
0.			1	QENEU244	2.5	76	77	73	0
	230 Mk III	Falex	2	QENEU160	2.5	66	72	57	0
			3	QENEU563	2.5	64	69	58	0
			1	19 60685	2	73	150		0.0
	230 Mk IV <sup>3</sup>	Alcor	2	19 60684	2	73	187		0.0
			3	19J74466	2	75	67		0.0
4			1	19 60686	2	73	68		250.1
	000 MIL 11/2	Alee#	2	19160688	2	74	82		2.7
	230 IVIK IV <sup>3</sup>	AICOL	3	19 60681	2	73	73		2.5
			4	19J74464	2	77	77		1.0

# Table 13. Results from Preliminary Interlaboratory Study for FLUID BUsing D3241 with 275 ℃ Operating Temperature

Lah	D3241	Tube	Ren	Heater	VTR	Max S	oot Thick	ness <sup>2</sup> (nm)	٨P
No.	Model	Mnfr	No.	Tube S/N	Code <sup>1</sup>	ITR	ETR	MWETR	(mmHg)
			1	TGWJY112	2	47	47		0.0
	230 Mk III	Falex	2	TJZJY145	1.5	52	44		0.7
0			3	TKUJY138	2	58	74		0.2
0			1	TGWJY768	1.5	46	57		2.3
F400	Falex	2	TGAJY185	1.5	36	58		0.5	
			3	TGQJY832	1.5	32	40		0.5
			1	SFYIX055	1	37	37		0.1
	230 Mk IV	Falex	2	SFRIX372	1	36	46		0
0			3	SGAIX195	3	79	85		0
9			1	19 62801	1A	>85	54		0.1
F400	Alcor	2	19 62764	1.5	36	40		0.8	
			3	19 62762	1	46	46		0

#### Table 13. Results from Preliminary Interlaboratory Study for FLUID B Using D3241 with 275 % Operating Temperature (Cont.)

<sup>1</sup>VTR codes of "<" or ">" are reported as -/+ 0.5 color unit.

<sup>2</sup> Metrology values reported in red were measured at UDRI.

<sup>3</sup> Participant laboratory ran tests with the same model of D3241 apparatus, however, unique serial number units were used for each set of replicates.

<sup>†</sup> Participant laboratory ran duplicate ITR, ETR, and MWETR readings, the median value from the two readings is reported.

## Environmental, Health, and Safety Assessment

It was requested that UDRI make a first attempt at characterizing the environmental, health, and safety (EHS) aspects of the candidate reference fluid(s). Haltermann Solutions was consulted and kindly produced a draft safety data sheet (SDS) for Fluids A and B, which are the most promising candidate mixtures, i.e., Exxsol D80 with hexylamine, dimethyl aniline, and diphenyl disulfide. A copy of the SDS can be found in Appendix B of this report.

## **Transition Plan**

The original RFP requested the development of a transition plan for any potential reference fluid(s). Again, UDRI consulted with Haltermann Solutions—a trusted manufacture of specialty fuels and test/reference fuels for industry—with regard to product feasibility. Haltermann Solutions believe it is feasible to produce a reference fluid(s) according to the specifications give in this report. Their assessment is based on prior experience and includes consideration of: the procurement of aliphatic solvent, blending the instigating mixture with the solvent, and containerizing the reference fluid blend at appropriate volumes (~1 L) for market. None of our discussions addressed cost

analysis, e.g., pricing and market analysis, as this is outside the scope of CRC and this project.

In addition to commercial production of the reference fluid, it is suggested that the concept of a reference fluid be brought before an appropriate commercial standards organization, e.g., ASTM and EI, so that consensus can be achieved within the industry. While UDRI does not currently intend to bring this concept to ASTM or EI directly, we are open to working with parties who would like to further the concept of a reference fluid for commercial standard approval.

# CONCLUSIONS

We have reported on the development of a reference fluid for use with ASTM D3241. The original observations and development, conducted by UDRI, were performed using a single Mark III Alcor JFTOT<sup>®</sup> with Falex heater tubes. Results indicate that a mixture of nitrogen and sulfur containing heteroatomic compounds can be added to an aliphatic solvent to produce a consistent, and reproducible level of deposition—and a detectible amount of pressure difference with the same solution—at 275°C using the ASTM D3241 method. The instigating heteroatomic compounds, i.e., hexylamine, dimethyl aniline, and diphenyl disulfide, and solvents, e.g., Exxsol D80, are easily obtainable at laboratory quantities and at the appropriate purity for direct use. The mixture appears to be stable over an extended period of storage (12 weeks at 43°C).

Preliminary interlaboratory study of both a high (Fluid A) and low (Fluid B) concentration reference fluids indicates excellent agreement for pass/fail surface deposit results; however, absolute deposit thickness vary significantly. While outside the scope of this work, the data collected in the pre-ILS could be used to help determine repeatability (r) and reproducibility (R) of the D3241 method directly. Regardless, the high concentration fluid consistently produced failing results >>85 nm deposit thickness, while the low concentration fluid produced deposits over a range of about 30 to 70 nm. Pressure drop results were more significant for the high concentration reference fluid. Alternatively, it was found that significant pressure drop could be generated using an N & S mixture at 300°C.

# ACKNOWLEDGEMENTS

The authors thank the following list of individuals and corporations for their support in the preliminary interlaboratory study:

Company	Individuals				
Air BP	Alisdair Clark	Michael Zahnhausen			
Chevron	Doug Cyr	Krege Christison			
DLA-E	Mike Domen				
ExxonMobil Research and Engineering	Dan Kadlecek				
NAVAIR	Andy McDaniel	Kevin Bowes			
Nobil Petroleum Testing	Madi Mohtadi				
PAC	Gordon Chiu	David Anderson			
QETE, Canada	Nathalie Gaudet	Marie Robichaud			
SwRI	Tim Kidwell				

The authors thank the valuable discussions and SDS contribution of Indresh Mathur of Haltermann Solutions. The authors thank the CRC technical panel for useful suggestions and feedback. Finally, the authors thank Erik Weber, Tim Edwards, and Paul Wrzesinski of the Fuels and Energy Branch (RQTF) of the Air Force Research Laboratory (AFRL) for use of AFRL facilities throughout this project (CRADA No. 10-223-RZ-01).

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# APPENDIX A: PRE-ILS PARTICIPANT INSTRUCTIONS AND RESULTS TEMPLATE

Partici	pant Insti	ructions	5:									
Thank yo not all pa i.e., do n there are	u for particip articipants wil ot combined any questior	ating in this I receive bo Fluid A and Is about thi	s pre-ILS study. oth fluids. These Fluid B. Please s study, or your	As a participan e fluids contain run all fluid sar role in it, plea	t you will receive o different levels of nples according to se direct any inqui	up to two active ing ASTM D3 ries to: Dr.	candidate fluids gredient, so pleas 241-19 using the . Zach West (zwe	(labeled 'Fluid se do not co-m operating con sst1@udayton.	A' and 'Fluid B' hingle different hditions given b edu, ph: (937)	'); note that t fluid types, pelow. If -255-4062).		
1)	Please fill	in <b>all</b> info	ormation reg	garding <b>exp</b>	erimental setu	up and t	est results or	n the " <b>User</b>	Data" work	ksheet of th	iis file (see example below).	
2)	Each fluid s	hall be <u>ru</u>	n in triplicate	e using the sa	ime experiment	al setup,	i.e., on the sa	me instrume	nt, using a n	ew heater to	be of the same manufacture for e	each run.
3)	Instrumer	nt operat	ing conditio	ons (for all r	uns) are as foll	ows:						
		Temper	ature = 275	°C								
		Flow Ra	te = 3.0 mL	/min								
		Test Du	ration = <b>150</b>	minutes (2	.5 hours)							
4)	Evaluate h	eater tul	bes using as	many evalu	, ation techniqu	ues as ar	e available to	vou and re	eport the re	sults in the	provided spreadsheet.	
5)	Please shin	all heater	r tuhe snecim	ens hack to I	IDRI once vou h	ave finis	hed performin	g all testing	(Shin to: AT	TN <sup>.</sup> 7ach We	st UDBI 1529 Brown St. Davton	OH USA 45469-0043)
6)	Email this	tost rosu	lt snreadsha	pet back to	zwest1@uday	ton edu						
7)	Any romai	ning tost	fluide movel	a disposed	of by the part	icinant i	n accordance	with your	organizatio	nc policios	and procedures	
/)	Any remai	ining test	Thulus Thay I	je uisposeu	of by the part			e with your	organizatio	nis policies		
EXAMPL	E DATA EN	NTRY:										
	Instru	ment	Poplicato			Hea	ater Tube			Standard S	Spot Thickness (nm)	
Sample	Model	S/N	No.	Run Date	$\Delta P$ (mmHg)	Mnfr	S/N	(Annex A1)	ITR (Annex A2)	ETR (Annex A3)	MWETR (Annex A4)	Notes / Comments
			1	2-Dec-19	2.3		ZBJIXOPO	4	156	163		
Fluid A	230 Mk III	741-0000	2	2-Dec-19	9.0	Falex	SB1IX379	<3A	158*	162		ITR gave 'N/A' reading
			3	3-Dec-19	3.5		SBJIY884	<3	160	159		

ASTM	STM D3241 Experimental Setup and Test Results											
	Instrum	nent	Deplicato	Dup	٨D	Heat	er Tube	VTP	Standard	l Spot Thickr	ness (nm)	
Sample	Model	s/N	No.	Date	ΔP (mmHg)	Mofr	S/N	(Δηρεχ Δ1)	ITR	ETR	MWETR	Notes / Comments
	Model	5/11		Date	(	IVIIIII	5/11	(AIIIIEX AI)	(Annex A2)	(Annex A3)	(Annex A4)	
			1									
Fluid A	230 Mk III		2			Falex						
			3									
			1			ļ						
Fluid A	230 Mk IV		2			Alcor						
			3									
			1									
Fluid A	F400		2			Falex						
			3									
			1									
Fluid B	230 Mk III		2			Falex						
			3									
			1			Ļ						
Fluid B	230 Mk IV		2			Alcor						
			3									
			1									
Fluid B	F400		2			Falex						
			3									

# APPENDIX B: DRAFT SAFETY DATA SHEET (SDS)



Safety Data Sheet according to Federal Register / Vol. 77, No. 58 / Monday, March 26, 2012 / Rules and Regulations Issue date: 06/07/2020

SECTION 1: Identification	
1.1 Identification	
Product form	· Mixture
Trade name	: JETOT Calibration Fluid
1.2 Performended use and restrictions on	
No additional information available	use
1.3. Supplier	
Haltermann Solutions <sup>the</sup> 15600 West Hardy Rd. Houston, TX 77060 - USA T 1-800-969-2542 - F 281-457-1469 <u>mhoveraker@jhaltermann.com</u>	
1.4. Emergency telephone number	
Emergency number	: 24 HR CHEMTREC: 1-800-424-9300; Emergency Assistance: 1-800-969-2542 (8 AM to 5 PM CDT)
SECTION 2: Hazard(s) identification	
2.1. Classification of the substance or mixt	ure
GHS US classification	
Flammable liquids Category 4 H227 Combustit	ole liquid
Aspiration hazard Category 1 H304 May be fat	al if swallowed and enters airways
Full text of H statements : see section 16	
2.2. GHS Label elements, including precaut	ionary statements
GHS US labeling	,
Hazard pictograms (GHS US)	
Signal word (GHS US)	: Danger
Hazard statements (GHS US)	: H227 - Combustible liquid H304 - May be fatal if swallowed and enters airways
Precautionary statements (GHS US)	<ul> <li>P210 - Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.</li> <li>P280 - Wear protective gloves/protective clothing/eye protection/face protection.</li> <li>P301+P310 - If swallowed: Immediately call a poison center or doctor.</li> <li>P331 - Do NOT induce vomiting.</li> <li>P370+P378 - In case of fire: Use media other than water to extinguish.</li> <li>P403+P235 - Store in a well-ventilated place. Keep cool.</li> <li>P405 - Store locked up.</li> <li>P501 - Dispose of contents/container to hazardous or special waste collection point, in accordance with local, regional, national and/or international regulation.</li> </ul>
2.3. Other hazards which do not result in cl	assification
No additional information available	
2.4. Unknown acute toxicity (GHS US)	
Not applicable	
<b>SECTION 3: Composition/Information</b>	on ingredients
3.1. Substances	
Not applicable	
3.2. Mixtures	

Name	Product identifier	%
Petroleum distillates, hydrotreated light	(CAS-No.) 64742-47-8	≥ 99
n-Hexylamine	(CAS-No.) 111-26-2	0.00125 – 0.0025

06/07/2020

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Name	Product identifier	%
	(CAS-No.) 882-33-7	0.00125 - 0.0025
3,5-Dimethylaniline	(CAS-No.) 108-69-0	0.00125 – 0.0025

Full text of hazard classes and H-statements : see section 16

SECTION 4: First-aid measures		
4.1. Description of first aid measures		
First-aid measures general	: Never give anything by mouth to an unconscious person. If you feel unwell, seek medical advice (show the label where possible).	
First-aid measures after inhalation	: Allow affected person to breathe fresh air. Allow the victim to rest.	
First-aid measures after skin contact	: Remove affected clothing and wash all exposed skin area with mild soap and water, followed by warm water rinse.	
First-aid measures after eye contact	: Rinse immediately with plenty of water. Obtain medical attention if pain, blinking or redness persists.	
First-aid measures after ingestion	: Rinse mouth. Do NOT induce vomiting. Immediately call a poison center or doctor/physician.	
4.2. Most important symptoms and effects	(acute and delayed)	
Potential Adverse human health effects and symptoms	: Based on available data, the classification criteria are not met.	
4.3. Immediate medical attention and speci	al treatment, if necessary	
No additional information available		
SECTION 5: Fire-fighting measures		
5.1. Suitable (and unsuitable) extinguishing	j media	
Suitable extinguishing media	: Foam. Dry powder. Carbon dioxide. Water spray. Sand.	
Unsuitable extinguishing media	: Do not use a heavy water stream.	
5.2. Specific hazards arising from the chem	ical	
Fire hazard	: Combustible liquid.	
Explosion hazard	: May form flammable/explosive vapor-air mixture.	
5.3. Special protective equipment and prec	autions for fire-fighters	
Firefighting instructions	: Use water spray or fog for cooling exposed containers. Exercise caution when fighting any chemical fire. Prevent fire-fighting water from entering environment.	
Protection during firefighting	: Do not enter fire area without proper protective equipment, including respiratory protection.	
SECTION 6: Accidental release measu	res	
6.1. Personal precautions, protective equip	ment and emergency procedures	
General measures	: Remove ignition sources. Use special care to avoid static electric charges. No open flames. No smoking.	
6.1.1. For non-emergency personnel		
Emergency procedures	: Evacuate unnecessary personnel.	
6.1.2. For emergency responders		
Protective equipment	: Equip cleanup crew with proper protection.	
Emergency procedures	: Ventilate area.	
6.2. Environmental precautions		
Prevent entry to sewers and public waters. Notify at	uthorities if liquid enters sewers or public waters.	
6.3. Methods and material for containment and cleaning up		
Methods for cleaning up	: Soak up spills with inert solids, such as clay or diatomaceous earth as soon as possible. Collect spillage. Store away from other materials.	
6.4. Reference to other sections		
See Heading 8. Exposure controls and personal pro	tection.	
SECTION 7: Handling and storage		
7.1. Precautions for safe handling		
Additional hazards when processed	: Handle empty containers with care because residual vapors are flammable. Keep away from heat/sparks/open flames/hot surfaces No smoking.	

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Precautions for safe handling	: Wash hands and other exposed areas with mild soap and water before eating, drinking or smoking and when leaving work. Provide good ventilation in process area to prevent formation of vapor. No open flames. No smoking.
7.2. Conditions for safe storage, including	any incompatibilities
Technical measures	: Proper grounding procedures to avoid static electricity should be followed.
Storage conditions	: Keep only in the original container in a cool, well ventilated place away from : Heat sources, Ignition sources, Incompatible materials. Keep container closed when not in use. Keep in fireproof place.
Incompatible products	: Strong bases. Strong acids.
Incompatible materials	: Sources of ignition. Direct sunlight. Heat sources.

### SECTION 8: Exposure controls/personal protection

3.1. Control parameters	
JFTOT Calibration Fluid	
No additional information available	
Petroleum distillates, hydrotreated light (64742-47-8)	
USA - OSHA - Occupational Exposure Limits	
OSHA PEL (TWA) (ppm)	500 ppm
n-Hexylamine (111-26-2)	
No additional information available	
(882-33-7)	
No additional information available	
3,5-Dimethylaniline (108-69-0)	
No additional information available	

#### 8.2. Appropriate engineering controls

No additional information available

8.3. Individual protection measures/Personal protective equipment

#### Personal protective equipment:

Avoid all unnecessary exposure.

#### Hand protection:

Wear protective gloves.

#### Eye protection:

Chemical goggles or safety glasses

#### **Respiratory protection:**

Wear respiratory protection.

#### Other information:

Do not eat, drink or smoke during use.

SECTION 9: Physical and chemical properties		
9.1. Information on basic	physical and chemical properties	
Physical state	: Liquid	
Appearance	: Clear, colorless liquid.	
Color	: Colorless	
Odor	: Petroleum-like odour	
Odor threshold	: No data available	
рН	: No data available	
Melting point	: No data available	
Freezing point	: No data available	

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Boiling point	: 208 – 236 °C (406°F - 457°F)
Flash point	: 82 °C (180°F) [ASTM D-93]
Relative evaporation rate (butyl acetate=1)	: 1.8
Flammability (solid, gas)	: No data available
Vapor pressure	: 0.013 kPa (0.1 mm Hg) at 20 °C
Relative vapor density at 20 °C	: No data available
Relative density	: 0.795 (at 15.6 °C)
Specific gravity / density	: 794 kg/m <sup>3</sup> (6.63 lbs/gal, 0.79 kg/dm <sup>3</sup> )
Solubility	: No data available
Partition coefficient n-octanol/water (Log Pow)	: No data available
Auto-ignition temperature	: 225 °C (437°F)
Decomposition temperature	: No data available
Viscosity, kinematic	: 2.18 mm <sup>2</sup> /s (2.18 mm2/sec) at 25°C
Viscosity, dynamic	: No data available
Explosion limits	: 0.6 – 5.1 vol %
Explosive properties	: No data available
Oxidizing properties	: No data available

#### 9.2. Other information

No additional information available

SECTION 10: Stability and reactivity		
10.1. Reactivity		
No additional information available		
10.2. Chemical stability		
Combustible liquid. May form flammable/explosive va	apor-air mixture.	
10.3. Possibility of hazardous reactions		
Not established.		
10.4. Conditions to avoid		
Direct sunlight. Extremely high or low temperatures.	Open flame. Overheating. Heat. Sparks.	
10.5. Incompatible materials		
Strong acids. Strong bases.		
10.6. Hazardous decomposition products		
fume. Carbon monoxide. Carbon dioxide. May release	se flammable gases.	
<b>SECTION 11: Toxicological information</b>		
11.1. Information on toxicological effects		
Acute toxicity (oral) :	Not classified	
Acute toxicity (dermal) :	Not classified	
Acute toxicity (inhalation) :	Not classified	
Petroleum distillates, hydrotreated light (6474	2-47-8)	
LD50 oral rat	> 5000 mg/kg	
LD50 dermal rabbit	> 2000 mg/kg	
LC50 inhalation rat (mg/l)	> 5.2 mg/l/4h	
n-Hexylamine (111-26-2)		
LD50 oral rat	670 mg/kg	
ATE US (oral)	670 mg/kg body weight	
3,5-Dimethylaniline (108-69-0)		
LD50 oral rat	707 mg/kg	
ATE US (oral)	707 mg/kg body weight	
Skin corrosion/irritation :	Not classified	
Serious eye damage/irritation :	Not classified	

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Respiratory or skin sensitization	: Not classified
Germ cell mutagenicity	: Not classified
Carcinogenicity	: Not classified
Reproductive toxicity	: Not classified
STOT-single exposure	: Not classified
STOT-repeated exposure	: Not classified
Aspiration hazard Viscosity, kinematic	<ul> <li>May be fatal if swallowed and enters airways.</li> <li>2.18 mm<sup>2</sup>/s (2.18 mm<sup>2</sup>/sec) at 25°C</li> </ul>
Potential Adverse human health effects and symptoms	: Based on available data, the classification criteria are not met.

#### SECTION 12: Ecological information

12.1. Toxicity

Petroleum distillates, hydrotreated light (64742-47-8)		
LC50 fish 1	45 mg/l (Exposure time: 96 h - Species: Pimephales promelas [flow-through])	
LC50 fish 2	2.2 mg/l (Exposure time: 96 h - Species: Lepomis macrochirus [static])	
n-Hexylamine (111-26-2)		
LC50 fish 1	53.8 – 59.6 mg/l (Exposure time: 96 h - Species: Pimephales promelas [flow-through])	
(882-33-7)		
LC50 fish 1	0.11 mg/l (Exposure time: 96 h - Species: Pimephales promelas [flow-through])	

#### 12.2. Persistence and degradability

JFTOT Calibration Fluid	
Persistence and degradability	Not established.

#### 12.3. Bioaccumulative potential

JFTOT Calibration Fluid		
Bioaccumulative potential	Not established.	
Petroleum distillates, hydrotreated light (64742-47-8)		
BCF fish 1	61 – 159	
n-Hexylamine (111-26-2)		
Partition coefficient n-octanol/water (Log Pow)	2.06	
(882-33-7)		
Partition coefficient n-octanol/water (Log Pow)	4.41	

#### 12.4. Mobility in soil

No additional information available

#### 12.5. Other adverse effects

Other information

: Avoid release to the environment.

SECTION 13: Disposal considerations	3
13.1. Disposal methods	
Product/Packaging disposal recommendations	<ul> <li>Dispose in a safe manner in accordance with local/national regulations. Dispose of contents/container to hazardous or special waste collection point, in accordance with local, regional, national and/or international regulation.</li> </ul>

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Additional information	: Handle empty containers with care because residual vapors are flammable.
Ecology - waste materials	: Avoid release to the environment. Hazardous waste due to toxicity.
SECTION 14: Transport information	
SECTION 14. Transport miormation	
Department of Transportation (DOT)	
In accordance with DOT	
Transport document description	: NA1993 Combustible liquid, n.o.s. (DISTILLATES (PETROLEUM), HYDROTREATED LIGHT), Comb Liq, III
UN-No.(DOT)	: NA1993
Proper Shipping Name (DOT)	: Combustible liquid, n.o.s.
	DISTILLATES (PETROLEUM), HYDROTREATED LIGHT
Class (DOT)	: Comb Liq - Combustible liquid
Packing group (DOT)	: III - Minor Danger
DOT Packaging Non Bulk (49 CFR 173.xxx)	: 203
DOT Packaging Bulk (49 CFR 173.xxx)	: 241
DOT Symbols	: D - Proper shipping name for domestic use only, or to and from Canada,G - Identifies PSN requiring a technical name
DOT Special Provisions (49 CFR 172.102)	<ul> <li>148 - Except for transportation by aircraft, when transported as a limited quantity or a consumer commodity, the maximum net capacity specified in §173.150(b)(2) of this subchapter for inner packaging may be increased to 5 L (1.3 gallons).</li> <li>IB3 - Authorized IBCs: Metal (31A, 31B and 31N); Rigid plastics (31H1 and 31H2); Composite (31HZ1 and 31HA2, 31HB2, 31HD2, 31HD2 and 31HH2). Additional Requirement: Only liquids with a vapor pressure less than or equal to 110 kPa at 50 C (1.1 bar at 122 F), or 130 kPa at 55 C (1.3 bar at 131 F) are authorized, except for UN2672 (also see Special Provision IP8 in Table 2 for UN2672).</li> <li>T1 - 1.5 178.274(d)(2) Normal</li></ul>
DOT Packaging Exceptions (49 CFR 173.xxx)	: 150
DOT Quantity Limitations Passenger aircraft/rail (49 CFR 173.27)	: 60 L
DOT Quantity Limitations Cargo aircraft only (49 CFR 175.75)	: 220 L
DOT Vessel Stowage Location	: A - The material may be stowed "on deck" or "under deck" on a cargo vessel and on a passenger vessel.
Other information	: Transportation Notes: Material is not regulated by the U.S. DOT for ground transportation within the U.S. if shipped in non-bulk packaging (<119 gallons).
Transport by sea	

Not regulated

#### Air transport

Not regulated

**SECTION 15: Regulatory information** 

#### 15.1. US Federal regulations

All components of this product are listed, or excluded from listing, on the United States Environmental Protection Agency Toxic Substances Control Act (TSCA) inventory

This product or mixture is not known to contain a toxic chemical or chemicals in excess of the applicable de minimis concentration as specified in 40 CFR §372.38(a) subject to the reporting requirements of section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 and 40 CFR Part 372.

#### 15.2. International regulations

#### CANADA

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Petroleum distillates, hydrotreated light (64742-47-8)		
Listed on the Canadian DSL (Domestic Substances List)		
n-Hexylamine (111-26-2)		
Listed on the Canadian DSL (Domestic Substances List)		
(882-33-7)		
Listed on the Canadian DSL (Domestic Substances List)		
3,5-Dimethylaniline (108-69-0)		
Listed on the Canadian NDSL (Non-Domestic Substances List)		

#### **EU-Regulations**

#### Petroleum distillates, hydrotreated light (64742-47-8)

Listed on the EEC inventory EINECS (European Inventory of Existing Commercial Chemical Substances)

#### n-Hexylamine (111-26-2)

Listed on the EEC inventory EINECS (European Inventory of Existing Commercial Chemical Substances)

#### (882-33-7)

Listed on the EEC inventory EINECS (European Inventory of Existing Commercial Chemical Substances)

#### 3,5-Dimethylaniline (108-69-0)

Listed on the EEC inventory EINECS (European Inventory of Existing Commercial Chemical Substances)

#### National regulations

Petroleum distilla	tes, hydrotreated	light (64742-47-8)	

Listed on the AICS (Australian Inventory of Chemical Substances)

- Listed on IECSC (Inventory of Existing Chemical Substances Produced or Imported in China)
- Listed on KECL/KECI (Korean Existing Chemicals Inventory)
- Listed on NZIoC (New Zealand Inventory of Chemicals)
- Listed on PICCS (Philippines Inventory of Chemicals and Chemical Substances)
- Listed on INSQ (Mexican National Inventory of Chemical Substances)
- Listed on the TCSI (Taiwan Chemical Substance Inventory)

#### n-Hexylamine (111-26-2)

Listed on the AICS (Australian Inventory of Chemical Substances)

- Listed on IECSC (Inventory of Existing Chemical Substances Produced or Imported in China)
- Listed on the Japanese ENCS (Existing & New Chemical Substances) inventory
- Listed on the Japanese ISHL (Industrial Safety and Health Law)
- Listed on KECL/KECI (Korean Existing Chemicals Inventory)
- Listed on NZIoC (New Zealand Inventory of Chemicals)
- Listed on PICCS (Philippines Inventory of Chemicals and Chemical Substances)

Listed on the TCSI (Taiwan Chemical Substance Inventory)

#### (882-33-7)

Listed on the AICS (Australian Inventory of Chemical Substances)

Listed on IECSC (Inventory of Existing Chemical Substances Produced or Imported in China)

- Listed on the Japanese ENCS (Existing & New Chemical Substances) inventory
- Listed on the Japanese ISHL (Industrial Safety and Health Law)
- Listed on KECL/KECI (Korean Existing Chemicals Inventory)
- Listed on NZIoC (New Zealand Inventory of Chemicals)
- Listed on PICCS (Philippines Inventory of Chemicals and Chemical Substances)
- Listed on INSQ (Mexican National Inventory of Chemical Substances)
- Listed on the TCSI (Taiwan Chemical Substance Inventory)

#### 3,5-Dimethylaniline (108-69-0)

Listed on the AICS (Australian Inventory of Chemical Substances)

Listed on IECSC (Inventory of Existing Chemical Substances Produced or Imported in China)

- Listed on the Japanese ENCS (Existing & New Chemical Substances) inventory
- Listed on the Japanese ISHL (Industrial Safety and Health Law)
- Listed on KECL/KECI (Korean Existing Chemicals Inventory)
- Listed on the TCSI (Taiwan Chemical Substance Inventory)

15.3. US State regulations

California Proposition 65 - This product does not contain any substances known to the state of California to cause cancer, developmental and/or reproductive harm

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Component	State or local regulations
n-Hexylamine(111-26-2)	U.S Massachusetts - Right To Know List; U.S New Jersey - Right to Know Hazardous Substance List; U.S Pennsylvania - RTK (Right to Know) List

#### SECTION 16: Other information

according to Federal Register / Vol. 77, No. 58 / Monday, March 26, 2012 / Rules and Regulations

Other information

: None.

#### Full text of H-phrases:

H227	Combustible liquid
H304	May be fatal if swallowed and enters airways

#### SDS US (GHS HazCom 2012)

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