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Friendly Cleaners**

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Chemical Aging of Environmentally Friendly Cleaners¹

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ABSTRACT

Use of cleaners in the manufacturing area demands bottles that will hold a sufficient amount of material and allow for easy and controlled dispensing by the operator without contamination or material leaching from the bottle. The manufacturing storage conditions are also a factor that may affect cleaner chemical integrity and its potential to leave a residue on the part.

A variety of squeeze bottles stored in mild (72°F, 10 % R.H., dark) and harsh (105°F, 50 % R.H., fluorescent lighting) conditions were evaluated to determine the effect of environment and bottle exposure on the chemical composition of TCA (1,1,1 trichloroethane) replacement solvents. Low Density Polyethylene (LDPE) bottles were found to be quite permeable to all the cleaners evaluated in this study indicating this bottle type should not be used in the manufacturing area. Fluorinated Polyethylene (FLPE) bottles showed little cleaner loss and change in cleaner chemical composition over time suggesting these bottles would be acceptable for use.

Chemical analysis indicates limonene-containing cleaners show increased non-volatile residue (NVR) content with storage under harsh conditions. Some cleaners use BHT (butylated hydroxytoluene) as stabilizer and to protect against limonene oxidation. Under harsh conditions, BHT was quickly depleted resulting in higher NVR levels.

INTRODUCTION

The vendors of environmentally friendly cleaners have established shelf life times for each of the cleaners based on containment within the manufacturer's sealed container. In the manufacturing area, these cleaners will be removed from the vendor container and placed in dispensers that will make hand wipe operations convenient. To ensure the exposure to the dispensing unit (squeeze bottles) and the manufacturing environmental conditions (temperature, humidity, light, and time) do not impose any adverse chemical aging on the cleaners, an aging study was initiated.

Many of the cleaners currently being evaluated for hand wipe operations in the manufacturing area contain the terpene hydrocarbon, limonene. It is well known that limonene readily oxidizes upon environmental exposure forming less volatile compounds. Conditions in this study were selected to not only mimic manufacturing conditions but also be of a sufficient harsh environment to produce oxidized limonene compounds.

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PLAN

CLEANERS, BOTTLES AND ENVIRONMENTAL CONDITIONS

Cleaning is accomplished by the removal of undesired material from a surface. Adhesion forces hold soils onto a surface. These forces can vary from very strong covalent bonds to relatively weak van der Waal's interactions. Some form of energy must be applied to overcome these adhesion forces if cleaning is to occur. Cleaning mechanisms can be identified as: dissolution, displacement, dispersion, reaction and mechanical removal.

Displacement of light soils can be accomplished with small amphiphilic solvents and alcohols. The solvents in these cases have a lower surface tension compared to the soil and must be partially but not fully soluble in the soil. Medium and heavy soils can be removed with moderately sized functional solvents. Solvents of this type partition out of the cleaner and into the soil. The soil softens, allowing surfactant emulsification and mechanical breakup where it would have been impossible.

Soil solubilization also occurs when the soil is completely soluble in the solvent. Soils and solvent must have very close solubility parameters. For hydrocarbon based (oily) soils straight hydrocarbons and water-immiscible solvents are used.

Six cleaners were selected from the candidates that are currently considered as acceptable alternative cleaners to TCA for hand wipe cleaning RSRM production components. These cleaners are listed in Table 1 along with a chemical description. Chemical features of these cleaners are shown in Figure 1.

Most of the cleaners contain the hydrocarbon limonene. Limonene is a ten carbon cyclic-aliphatic compound (terpene) with two sites of unsaturation. The percentage of limonene varies from 100 to 8 percent depending on the formulation. A few of these cleaners contain the stabilizer BHT (butylated hydroxytoluene) at various levels. BHT is an antioxidant that reacts with oxygen more readily compared to limonene. Once BHT is depleted from the cleaner, limonene will be the next target of oxidation.

Dipropylene glycol methyl ether (DPGME) along with 1TB2P (1-t-butoxy-2-propanol) and N-methyl pyrrolidone (MP) were other chemical components found in the cleaner formulations. The glycol ether and alcohol are used for displacing light soils and N-methyl pyrrolidone is known for its ability to soften paints. Two of the cleaners contain a mixture of more non-polar components, hydrocarbons. For the PFD cleaner, the hydrocarbons are a mixture with chain lengths from ten to fourteen carbons. The BA4 cleaner is also composed of a mixture of aliphatic hydrocarbons. This cleaner, however, contains hydrocarbons that are cyclic and branched with average chain lengths between nine and thirteen carbons.

Table1: Cleaners and Their Composition

Cleaners***	Abbreviation	Limonene	BHT	DPGME	HC	MP	1TB2P
BIOACT® PCG	PCG	X					
RE-ENTRY® PREPSOLV	PRP	X	X				
RE-ENTRY® PLUS4 SOLVENT	PL4	X	X	X		X	X
BIOACT® 113	BA1	X					X
PFT™ Solvent	PFD	X	X		X*		
BIOACT® 145	BA4			X	X**		
* = C ₁₀ to C ₁₄ hydrocarbons ** = mixed aliphatic hydrocarbons (C ₉ to C ₁₃ branched and cyclic). *** = all cleaners are manufactured by Petroferm except for PFT™ Solvent that is manufactured by PT Technologies							

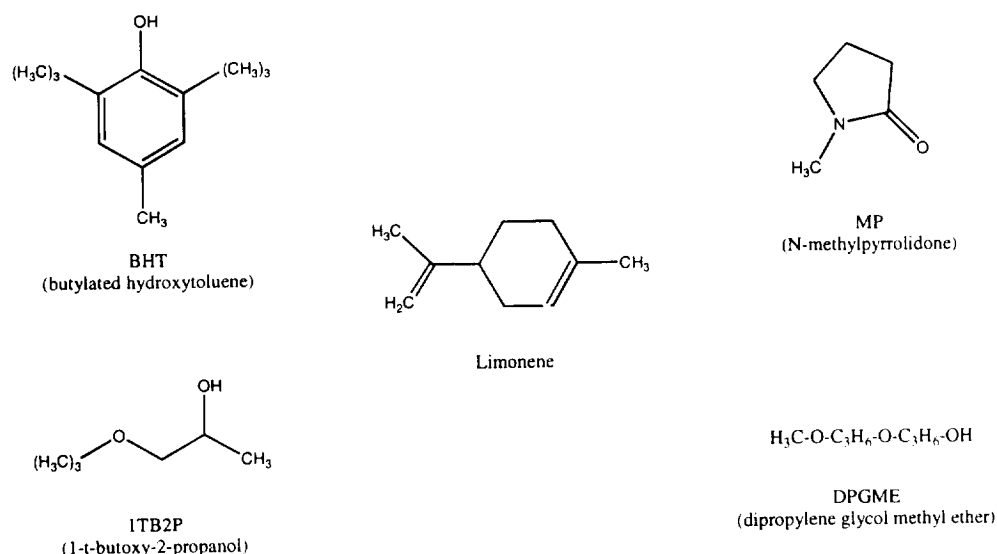


Figure 1: Chemical Structure of ODC Cleaner Components

Four bottles were evaluated in this study: LDPE (low density polyethylene), FLPE (Fluorinated High Density Polyethylene), Silgan (HDPE and Nylon) and Glass (baseline) bottles. LDPE bottles are used in the manufacturing area to contain alcohols. The FLPE bottles are currently used to contain TCA in the manufacturing area. Silgan bottles (manufactured by Silgan Plastic Corporation) were also evaluated. These bottles are composed of a HDPE (high density polyethylene) outer layer and a Nylon inner layer. For the LDPE, FLPE and Silgan bottles polypropylene caps and nozzles were used. The nozzles were cut to expose the cleaner contained in the bottle to the harsh or mild condition.

Glass bottles were used as a baseline. Glass Qorpak bottles (Fisher Catalog #03-320-11J) were fitted with Teflon closures and spouts so the cleaner would be exposed to the same atmosphere cleaners the squeeze bottles would see.

The storage conditions were selected to not only represent typical and worse case conditions found in the manufacturing areas but also in the worse case condition be of a sufficiently harsh environment to induce high levels of non-volatile residue (NVR). The mild (typical normal manufacturing area) environment was selected as $72 \pm 5^\circ\text{F}$, less than 10 % R.H. and samples stored in the dark. For harsh conditions the bottles were stored at $105 \pm 5^\circ\text{F}$, 50 % R.H. and under constant exposure to fluorescent lighting.

CHEMICAL ANALYSIS

Several methods of chemical analysis were conducted to monitor the effect aging has on the chemical properties of the cleaners. The methods used in this study include non-volatile residue, and moisture.

The NVR testing conducted on cleaners containing limonene is not an absolute evaluation of the non-volatile residues that will be seen on a production part. Instead, the NVR results should only be used to evaluate the purity of the material. The residue is an empirical measurement defined by the evaporation conditions (105°C) and defined as any material that does not evaporate after four hours in a forced draft oven. These cleaner residues may be the result of dissolved bottle materials (low molecular weight polymer products)/ bottle plasticizers or solvent degradation/ oxidation.

The water content was determined by a Karl Fischer titration method using pyridine-free reagents. The method measures water content by quantitatively titrating the water with a base-iodine-sulfur dioxide complex. Water consumption is determined by amperometric endpoint detection using a dual platinum wire electrode.

DISCUSSION

To ensure the NVR testing method would produce results that would be consistent throughout the study, a correlation between NVR and test conditions was made. A newly manufactured lot of PCG was compared with cleaner that had been stored in the manufacturing area for 6 months. Seven to ten milliliters were placed in a 75-ml aluminum dish and allowed to evaporate under temperatures ranging from ambient (20°C) to 130°C.

Figure 2 shows the effect of test temperature on NVR level. For the aged PCG, the ambient dried samples had a higher NVR percentage most likely due to low molecular weight oxidized limonene products. These low molecular weight compounds are present when the evaporation temperature is near ambient while at higher temperatures they evaporate. The NVR content for the aged PCG appears to stabilize between 100 and 110°C. Thus the temperature of 105°C was selected for NVR testing in this study.

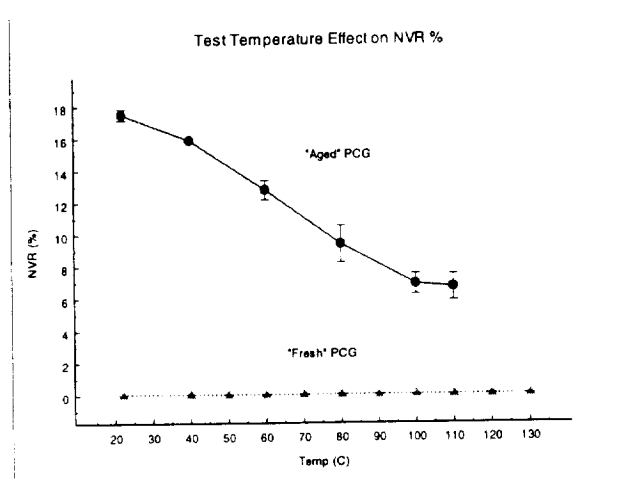


Figure 2: Percent NVR as a Function of Evaporation Temperature

The time that the samples were dried was also investigated during the development of the NVR test method. Figure 3 shows the NVR levels of the newly manufactured PCG and 6 months aged PCG ranging from a dry time of 10 minutes to 6 hours at 105°C. The fresh PCG NVR levels become stable after 2 hours while the aged PCG continues to lose weight. The weight loss over time is most likely due to a continued loss of semi-volatile oxidized compounds. From this preliminary testing, the NVR test method was selected as evaporation of a 10-milliliter sample of cleaner at 105°C for four hours in a forced draft oven.

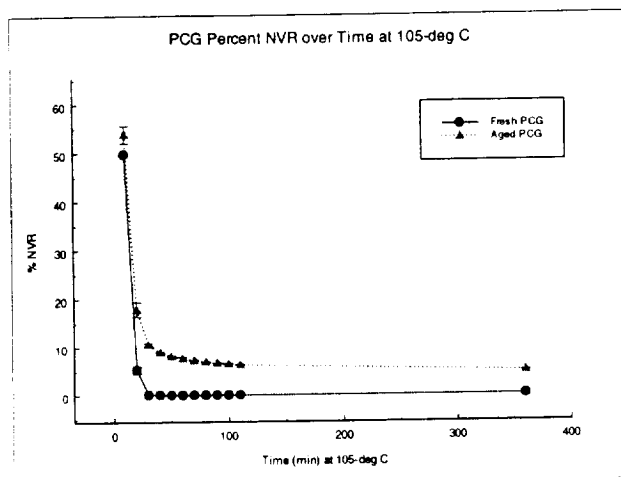


Figure 3: Percent NVR as a Function of Time at 105°C

The NVR content of the cleaners stored under harsh conditions in glass bottles over time is shown in Figure 4. The NVR level can be readily correlated with limonene content and BHT depletion. Both cleaners that contain limonene and no stabilizer (PCG and BA1) show initial higher levels of NVR compared to the other cleaners. Those cleaners that contain limonene and stabilizer show increased NVR levels as soon as the stabilizer is depleted. Stabilizer depletion for PFD was 3 weeks, for PRP four weeks and for PL4 the stabilizer was depleted by 9 weeks. The time to stabilizer depletion was dependent on both the stabilizer amount and limonene percentage in the cleaner. Those cleaners with no limonene (BA4) or very little (PFD) show very little NVR formation over 52 weeks.

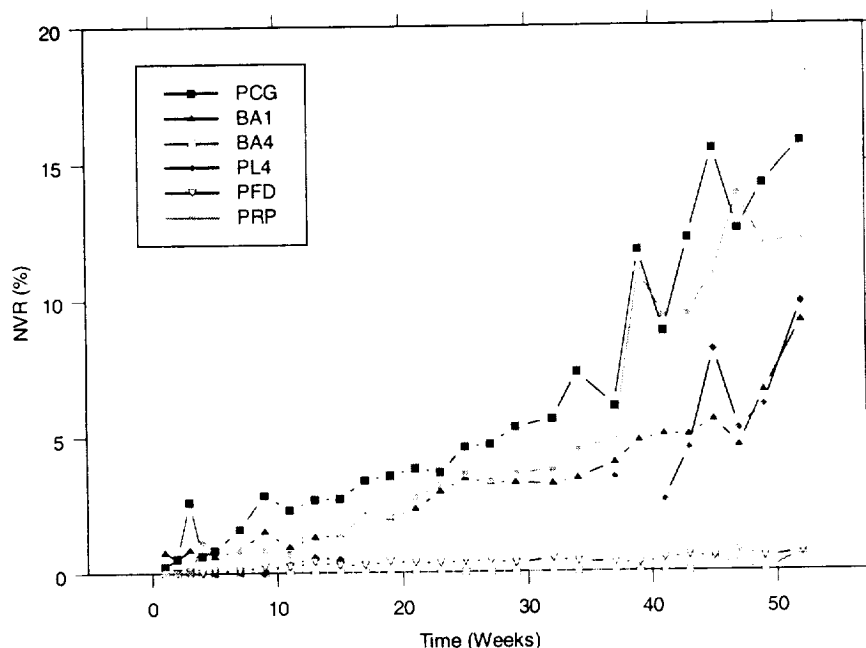


Figure 4: Percent NVR as a Function of Time under Harsh Conditions in Glass Bottles

The NVR content of the cleaners in glass bottles under mild is shown in Figure 5. As expected, only those cleaners with limonene and without stabilizer show any increase in NVR content. Those cleaners

with limonene and no stabilizer have higher NVR content at zero-time testing. Over time under mild conditions only these cleaners show an increase in NVR content since the stabilizer, BHT, prevents limonene oxidation and NVR formation. As expected, the NVR content for cleaners stored under mild conditions is lower than when stored under the harsh environment.

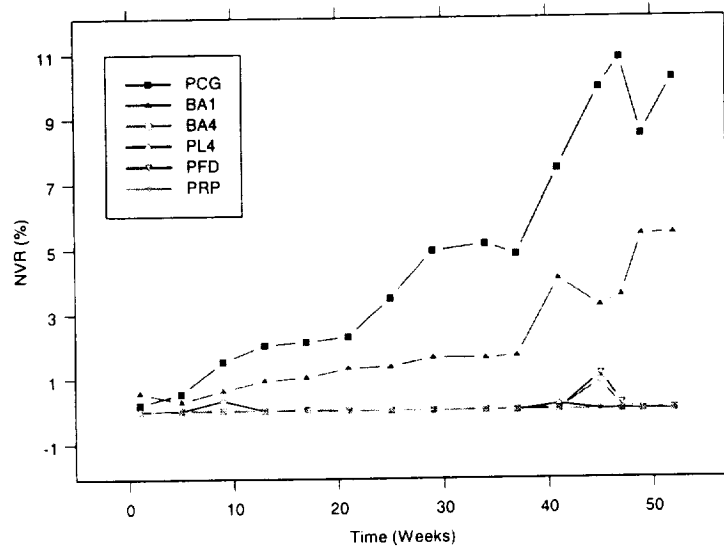


Figure 5: Cleaner NVR Content in Glass Bottles under Mild Conditions

Variation in NVR content due to bottle type is shown with the example of PCG under harsh conditions (Figure 6). LDPE bottles appear to be more permeable. Under the harsh conditions weight loss analysis shows PCG in the LDPE bottle diffuses out of the bottle quite readily. Moisture analysis of the PCG also shows water diffuses into the bottle as well. The NVR difference between glass and LDPE bottles may be attributed to the glass bottle larger spout opening and potentially the glass transparency.

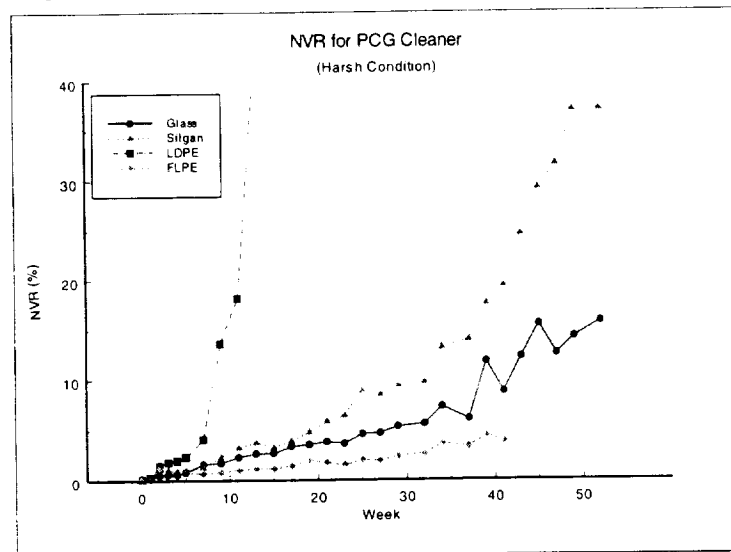


Figure 6: PCG NVR Content after 52 Weeks under Harsh Conditions

The moisture content of the cleaners in glass bottles stored under harsh conditions is shown in Figure 7. The cleaners with the higher moisture content (BA1, BA4 and PL4) all contain chemical

components that are hydrophilic in nature (DPGME and 1TB2P). Over time and 50 % relative humidity, these cleaners continue to pick up moisture. Other cleaners (PCG, PRP) contain large percentages of limonene that oxidizes over time and under harsh conditions to produce materials that are more hydrophilic in nature. Only PFD with very little limonene and a large percentage of hydrocarbons picks up little moisture over time.

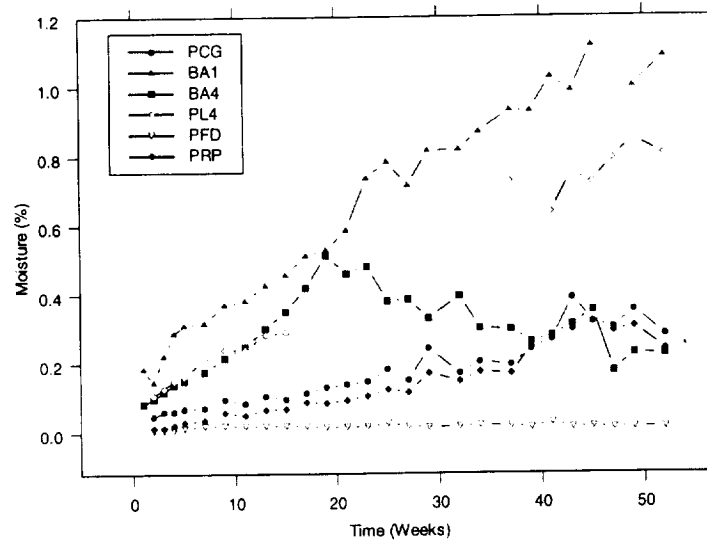


Figure 7: Cleaner Moisture Content under Harsh Conditions

Figure 8 shows the cleaner moisture content stored under mild conditions (less than 10 % relative humidity) in glass bottles. As observed under the harsh conditions, cleaners with hydrophilic components have higher levels of initial moisture and will gain more moisture over time with exposure to the atmosphere.

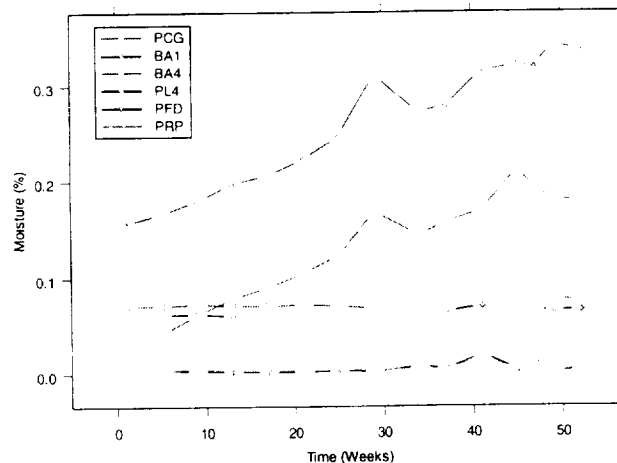


Figure 8: Cleaner Moisture Content under Mild Conditions

Like the NVR levels, cleaners stored in LDPE bottles show higher moisture content compared to the other bottles evaluated in this study. Figure 9 shows the moisture content of PL4 stored in the various bottles under harsh conditions. The glass bottles also have higher moisture content compared to the FLPE bottles and may be explained by the larger spout in the glass bottle allowing for an increased exposure to the atmospheric moisture.

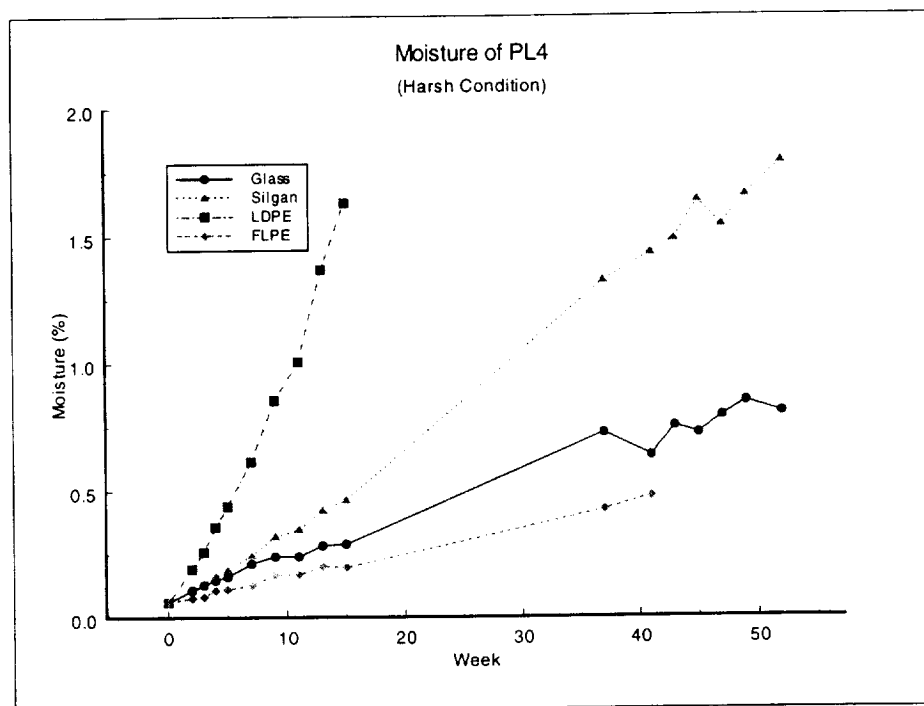


Figure 9: Plus-4 Moisture Content after 52 Weeks under Harsh Conditions

SUMMARY/CONCLUSIONS

The NVR content as measured by evaporation of ten milliliters at 105°C for 2 hours in a convection air oven is a method that can be used to monitor the purity of a cleaner and is not an absolute evaluation of non-volatile residues that will be seen on a production part. The NVR content is dependent not only on the amount of limonene present in the cleaner but also on the presence of a stabilizer (BHT). The storage of cleaners in high humidity, high temperature and fluorescent lighting also contributes to the oxidation of limonene. If stored in a mild or production representative environment the stabilized limonene based cleaners showed little change in NVR content.

Cleaners that contain moisture sensitive compounds (1TB2P and DPGME) initially have higher levels of water. The moisture content increases, as samples are stored under high humidity conditions. If stored in a mild or production representative environment there is little change in moisture content over 4 months.

A cleaner's susceptibility to moisture and NVR formation is also dependent on the type of storage bottle. The permeability of LDPE bottles to moisture prohibits their use in a manufacturing environment. FLPE bottles are less susceptible to moisture and thus are a good candidate.

Subsequent to this test effort the solvents PLUS-4 and PF Degreaser were down-selected for hand cleaning applications in the manufacturing centers. Relative to these solvents, the following recommendations were made to the manufacturing centers:

- FLPE squeeze bottles should be utilized for storage in the manufacturing centers.
- The squeeze bottle shelf life of PLUS-4 and PF Degreaser is at least one year of storage under a humidity, temperature, and lighting environment similar to manufacturing conditions. (Testing will ensue to determine chemical stability beyond one year.)