

Exhibit 1370 State of Minnesota v. 3M Co., Court File No. 27-CV-10-28862

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The function of most organic coatings is to protect and/or decorate substrates. Surface detects such as craters, sags and thick edges mar appearance and create weak spots which decrease protection. Many surface defects arise from resin or

Many surface detects arise from resin or pigment flow in the paint film after it is applied. Such movement is caused primarily by surface tension forces with the main force opposing it being viscosity. Preventing defects will allow the coating formulator additional time to spend on the more productive tasks of creating functional coatings with improved profitability. profitability.

This brochure discusses how to eliminate or reduce surface defects by the control of surface tension.

### **BENEFITS OF FLUORAD** FLUOROCHEMICAL SURFACTANTS

Curing surface defects is never easy. Ideally solutions are developed from a knowledge of the cause of the defect. Unfortunately, diagnosis is cause of the defect. Unfortunately, usignous is often difficult since the coating supplier is seldom on site when the defect is observed and substrate cleanliness can be inadequate and/or irregular. The maintenance of coating surface tension values at low levels with Fluorad fluorochemical surfacetants

can help produce coatings capable of being used in "less than perfect" industrial applications. The formulator will benefit by maintaining a quality "trouble free" image and reducing unproductive problem solving.

The use of additives in the paint and coating industry has been gaining greater acceptance as their benefits become increasingly difficult to reproduce with modifications of the base resins or solvent system. Much development time is still spent in solvent and resin permutation (to reduce surface tension values) when the use of Fluorad fluorochemical surfactants could achieve the desired effect. The use of lower cost solvents and resins frequently offsets the increase in cost of the surfactant.

Ingredient mischarge can happen in the best run factory; a Fluorad fluorochemical surfactant has been used on more than one occasion to reduce scrap costs by rescuing a paint overcharged with silicone defoamer.

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## FLUORAD FLUOROCHEMICAL SURFACTANTS IN COATINGS

Fluorad fluorochemical surfactants were first used in a major coating application in 1958. A patent awarded to H.C. Geen of the Simoniz Company claimed that 3M company's fluorosurfactants conferred superior leveling to dry bright aqueous conferred superior leveling to dry bright aqueous emulsion floor wax systems. Since that time, fluorosurfactants have been universally adopted in both household and institutional floor polish systems. They provide the necessary leveling and wetting performance over floors covered with "old" polish, or surfaces contaminated with low energy films such as grease or sillcone resins. The low concentration of Fluorad fluorochemical surfactant needed for good performance significantly reduces v. P. ... needed for good performance significantly reduces detrimental effects, such as "black hee!" marks, frequently seen with high levels of conventional surfactants.

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Just as the hydrophobic moleties in Fluorad surfactants enable them to function as highly efficient surfactants enable them to function as inging endocent additives in aqueous coatings, it was soon recognized that fluorochemicals should be capable of modifying surface tension in organic systems by virtue of the oleophobicity of their fluorochemical molety. By careful choice of the solubilizing group in the molecule, 3M chemists have been able to design Fluorad products to function as surface active agents in many solvents and resins. Surface tension control in organic systems is now

Surface tension control in organic systems is now possible, not only during the application of a solvent based coating, but also during the dynamic phase of drying and resin polymerization. The maintenance of low surface tension values throughout the drying phase will eliminate, or reduce, steep surface tension pendionate which are frequently responsible for the gradients which are frequently responsible for the formation of many coating defects such as floating, orange peeling, and fish eyes.

orange peeiing, and tisn eyes. In an industrial situation it is not uncommon for surface preparation to be erratic. Low surface tension values will help considerably in minimizing the effect of such variation on coating appearance by improving the ability of the coating to wet and spread on the substrate. These surfactants are used extensively to reduce the surface tension of both extensively to reduce the surface tension of to organic and aqueous based coatings. Spot contamination in the form of fingerprints, roller grease, condensation drip, and even gross contamination from a mischarge of a silicone defoamer, can be overcome by the use of fluorochemical surfactants.

Consistent product performance is one step closer when Fluorad surfactants are used.

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## FLUOROCARBON AND HYDROCARBON SURFACTANTS

A surfactant (surface active agent) can be defined as:

A material which concentrates at the surface of the liquid in which it is dissolved, or at the interface of a liquid and another immiscible liquid or solid.

Since many polymers and oligomers are themselves surface active, they compete for space at an interface. Their presence can make it difficult to predict the behavior of any surfactant in specific resin systems.

Another definition of a surfactant is: A chemical comprised of two parts of widely differing polarity and solubility in liquid media.

In general, surface active agents have limited solubility in the liquids in which they are used. Both definitions are useful in highlighting the major differences between fluorochemical and hydrocarbon surfactants.

Both classes of surfactants act in a similar fashion in aqueous systems. The insoluble portion of the molecules—the hydrocarbon and the fluorocarbon hydrophobic chain—both orientate at the liquid surface with the hydrocarbon or fluorocarbon tail of the molecule in the gas phase and the more polar portion in the aqueous phase.

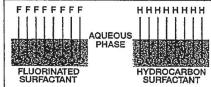


Figure 1. Surfactant orientation in equeous coatings.

Figure 1. Suffactant orientation in equeous ceatings. There is, however, a significant difference in efficacy due to the stronger electron withdrawing power of the fluorine atom. Surface tension values as low as 16 dynes/cm in aqueous systems are attainable with fluorocarbon surfactants at concentrations as low as .005%. This contrasts with a minimum value of about 25 dynes/cm at 1% with a typical hydrocarbon surfactant a typical hydrocarbon surfactant.

The small amount of Fluorad fluorochemical surfactant necessary in aqueous coatings reduces the tendency for floor coatings to develop "black heel" marks. In addition, the low use concentration in floor polish systems has only a small effect on more than the systems has only a small effect on manufacturing cost calculated on a per gallon basis.

. X The fluorocarbon and hydrocarbon tails on the molecules behave very differently in nonaqueous systems due primarily to the major differences in the solubility of the tails in the organic components in the coating. Typically, the hydrocarbon tails of conventional surfactants have sufficient solubility in organic paint systems whereby the chemical will not migrate to a liquid/gas interface to function as an efficient surface active agent. The reverse is the case with molecules having fluorocarbon tails. These moieties are not miscible with organic liquids, such as solvents or resins. By using the correct solubilizing group, 3M chemists have designed fluorochemicals which orientate at an organic interface to act as a surfactant (see Table 1 on page 10).

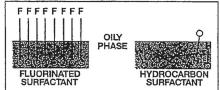
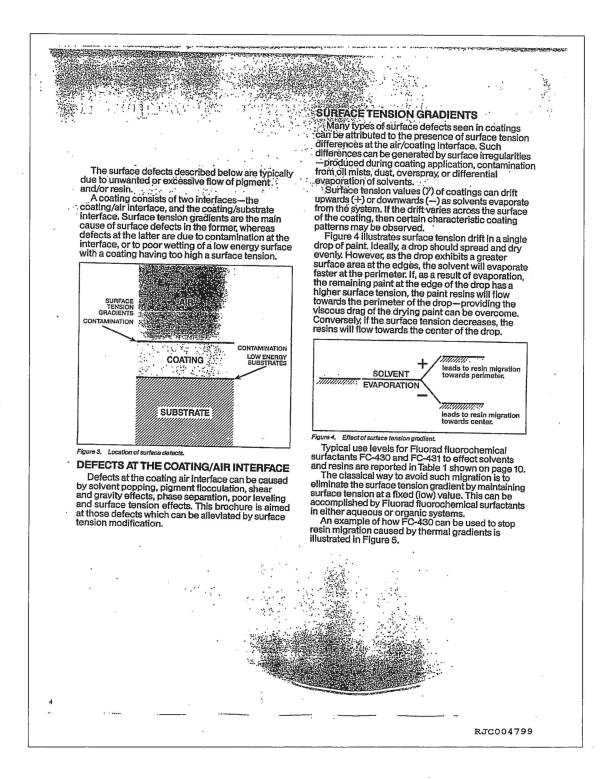
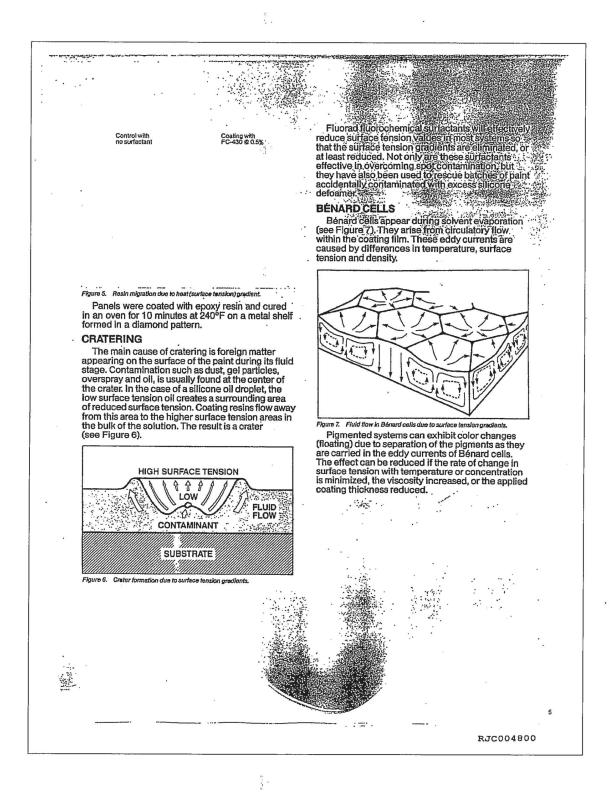


Figure 2. Surfactant orientation in organic coatings.

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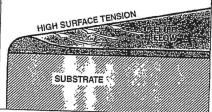
# **ORANGE PEELING**

Localized surface tension variations across the coating surface create slight mounds and dimples in the surface of the coating. Similar irregularities can also be observed when dewetting occurs. This effect, described as "orange peel," is sometimes desirable to hide substrate roughness in large objects. If orange peeling is undesirable, the effect can be reduced by the use of Fluorad surfactants to control the surface tension variation and improve substrate wetting. tension variation and improve substrate wetting, Increased viscosity to lower coating mobility will also reduce the problem.

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### **PICTURE FRAMING**

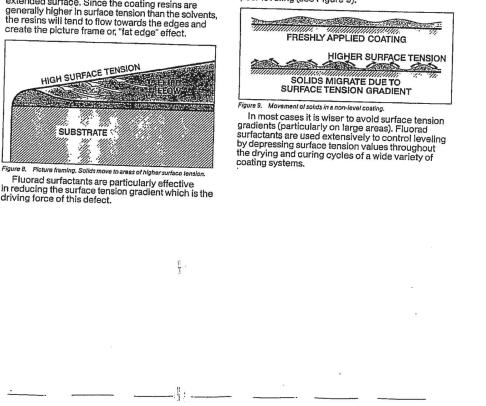
This common coating effect appears as a build up This common coating effect appears as a build up of paint at the edges of coated articles. It should not be confused with sagging, which occurs at the lower edges of vertical substrates. Picture framing (see Figure 8) is the result of surface tension gradients occurring at the edges of a substrate due to a faster rate of evaporation of the coating solvents at the extended surface. Since the coating resins are extended surface. Since the coating solvents at the extended surface. Since the coating resins are generally higher in surface tension than the solvents, the resins will tend to flow towards the edges and create the picture frame or, "fat edge" effect.



Fluorad surfactants are particularly effective in reducing the surface tension gradient which is the driving force of this defect.

# LEVELING

LEVELING Paradoxically, the leveling capability of a coating should be improved with high surface tension which tends to minimize the surface area (and hence smooth the surface) of the applied coating. Leveling defects caused by application methods such as brush marks and roller striations should be reduced if the system surface tension can be increased. However, the presence of a surface tension value—can also produce a leveling problem similar to those mentioned earlier. In a freshly applied non-level coating, surface tension gradients can be caused if the coating components have differing evaporation rates and different surface tension values. Less volatile components will evaporate slower in the valleys of the applied coating, and the converse for the coating at the peaks. The surface tension gradient will cause a flow of coating solids to the peaks—resulting in poor leveling (see Figure 9). poor leveling (see Figure 9).



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### DEFECTS AT THE COATING/SUBSTRATE INTERFACE

All substrates have a surface energy (tension). The pioneering work of Zisman established values for the surface energy of solids and although Zisman's work did not take into account the variations seen in surface energy due to surface roughness, the values never-the-less provide a foundation for the ranking of the difficulty of wetting various substrates.

TABLE 2. TYPICAL SURFACE ENERGY VALUES OF VARIOUS SURFACES

LIQUIDS											Dynes/cm mN/m		
Water		7											73
Lube Oil													29
Water Lube Oil . Silicone Oil	•		•	•	•					•	•	·	20
RESINS													
Liquid Epoxy Liquid Polyester Alkyd									1				48
Liquid Polyester													35
Alkyd													25
Polydimethylsiloxi	an	e		•					2		•		20
SOLIDS													
Phosphated Steel													43-56
Aluminum .										1			37-45
Tin Plate													35-45
Polyester		١,											43
Tin Plate Polyester Polyvinyl Chlor de	э.												39
Polystyrene						ï							33
Polystyrene Polyethylene Polytetrafluoroeth													31
Polytetrafluoroeth	vl	e	n	e	Ì							÷	18

A liquid will only wet and spread over a surface if the forces of attraction between the liquid and the substrate are greater than the cohesive forces within the liquid.

The concept of the "spreading coefficient" has been used to predict the ability of a liquid to

spontaneously wet and spread on a substrate. If Yuquid is the surface tension of the coating,  $\gamma_{\text{Sold}}$  is the surface energy of the substrate, and  $\gamma_{\text{US}}$  is the interfacial tension between the and 70s is the interfactant tension between the coating and the substrate, then the spreading coefficient SC is defined as: SC =  $\gamma_{Swid} - (\gamma_{Lwid} + \gamma_{Lw})$ . Spreading will only occur if this coefficient is a positive number. Defects will be prevented or a subset of  $\gamma_{Lwid}$  and  $\gamma_{Lwid}$ .

reduced if YLiquid and YLs are made as small as possible.

The minimum criteria for any coating to wet and spread on a solid is for the surface tension of the coating to be less than the surface energy of the substrate. Examination of Table 2 and comparison with Table 1 will provide an illustration of how Fluorad fluorochemical surfactants can assist in helping coatings wet and spread on challenging substrates.

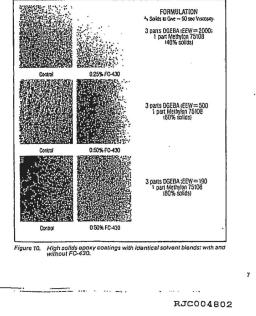
Similar conclusions can be drawn if the substrate is covered with a contaminating film of hydrocarbon or silicone oll. Only in this instance, the surface tension values of the oil film can be substituted for that of the solid substrate. Additional steps which can be taken to improve

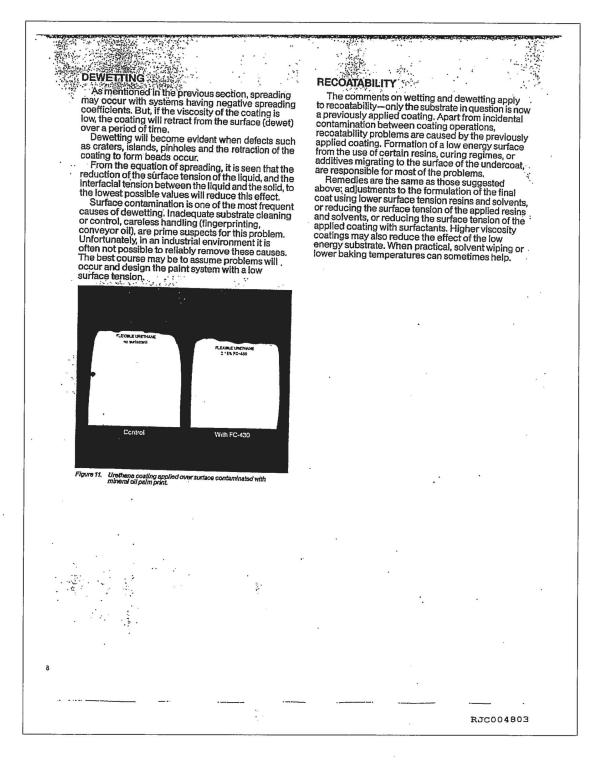
wetting and spreading are the replacement of resins and solvents with those having lower surface tension values and higher viscosities.

The energy expended during coating application and the degree of surface roughness will both influence spread of a coating on a surface and, if a coating can be made to spread, even temporarily, it will be possible to maintain a continuous film if the viscosity is sufficiently high.

However, if the movement to higher solids systems frequently limits viscosity modification or the choice of resins, the necessity of incorporating an efficient surfactant becomes the only practical option.

Figure 10 illustrates three epoxy-phenolic formulations of similar viscosities, but increasing solids content, coated on "contaminated" oily tin plate and baked. With no flow control agent added, the "conventional" 40% solids formulation based on the conventional 40% solids formulation based on diglycidyl ether of Bisphenol A (DGEBA) with an epoxy equivalent weight (EEW) of 2000, shows good coverage with some pinholes. When a lower equivalent weight DGEBA of 500 is substituted to achieve 60% solids, severe cratering is obvious. Total retraction into droplets results when a liquid DGEBA of EEW = 190 is substituted to reach 80% solids. When Fluorad surfactant FC-430 is added to each system, good wetting and leveling is observed in all cases.





The capability of Fluorad fluorochemical surfactants to be used as surfactants in organic media allows the coating formulator to reduce defects caused by surface tension variations in organic coatings as well as aqueous systems. Coatings with fewer defects translate to infrequent interruptions of the coating line and higher productivity, less rework and lower rework costs, greater reliability and improved quelity All these greater reliability and improved quality. All these factors imply savings and satisfied customers. A wide selection of Fluorad surfactants are

a vallable to assist the coating formulator (listed in . Table 3, page 11). The effectiveness and choice of the best Fluorad surfactant in coatings is dependent on the degree of its solubility/insolubility in the coating media. The surfactant should be active at the surface the moment the defact is about to form The surface the moment the defect is about to form. Thus it may be necessary to consider the solubility relationships of the surfactant at various pH, or in a solvent, a liquid resin, or any mixture of these at a variety of temperatures. With these variables, it is impossible to provide precise recommendations for the behavior of a surfactant to sure aget defect but Table 4 (page 10) is an appropriate starting point Table 4 suggests starting concentrations for

evaluation of these surfactants in the various coatings. The values in Table 4 are the percent concentration of surfactant, as supplied, taken on a weight basis.

An improvement in wetting and leveling has been An improvement in weater reducible coatings when observed in some water reducible coatings when Fluorad fluorochemical surfactant FC-171 has been blended with FC-430 or FC-431 in a 40/60 ratio and used at a level of 0.2% based on coating solids. Other blends of Fluorad surfactants may also prove useful in other systems.

Foaming can sometimes be reduced if FC-170-C and FC-171 can be used.

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**USE LEVELS** 

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The ranges of use concentration depend on the

Solvent vehicle used. Table 5 (page 11) assists in the solvent vehicle used. Table 5 (page 11) assists in the selection of an appropriate solvent. Typically, the use of Fluorad surfactants in aqueous media is between .005% and .02% based on resin solids. In water reducible coatings the level is between .05% and .3%, and in solvent coatings the level is between .1% and .7%, based on coating solids. To ensure the most effective use of surfactant,

It is recommended that a stock solution of the product be prepared prior to addition to the coating. Often, a 1%-10% solution is made. Instructions how to do this are given in the individual technical data sheets.

#### **3M AND COATINGS**

The 3M Company has had a long tradition of of various substrates with a wide variety of varishes, paints, adhesives, binders, sizes and resins. Programs are continually underway to improve coating performance and many of these will yield commercial products in the future.

Share your problems with us; 3M sales and technical service staff will work with you to solve them.

#### **3M Corporate Headquarters**

Industrial Chemical Products Division 3M Center Bldg. 223-6S-04 St. Paul, MN 55144-1000 800/541-6752 (Ordering Product & Pricing) 612/733-1683 (Literature Requests) 612/736-1394 (Telesales)

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CANADA 3M Canada, Inc. P.O. Box 5757, Terminal A London, Ontario N6A4T1 519/451-2500

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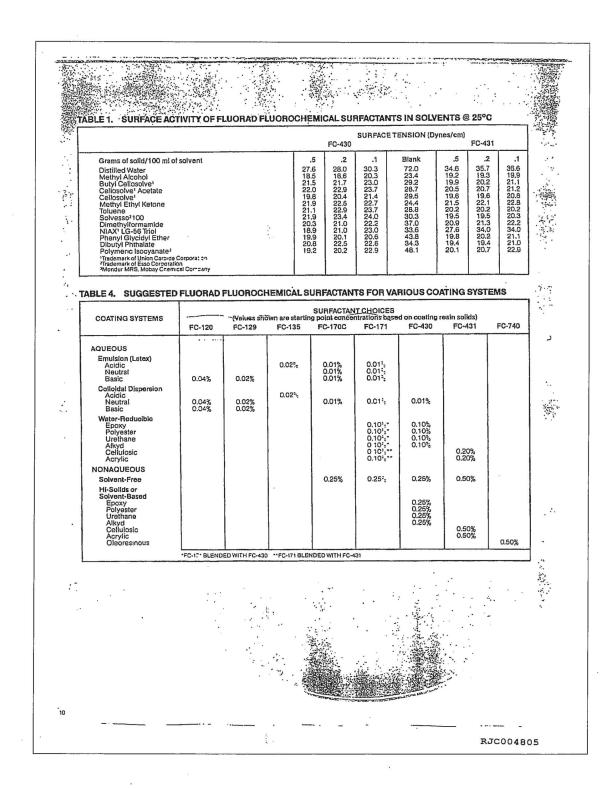


TABLE 3. TYPICAL PHYSICAL PROPERTI	ES OF	FLUOR	AD FLUO	ROCHEMIC	ALSURF	ACTANTS	5*		
PRODUCT GENERAL STRUCTURE OR CODE DESCRIPTION ( $R_1 = C_n F_{2n-1}$ )		TYPE	% ACTIVE	SPECIFIC	VISCOSI © 25C (c	TY FLA	SH POINT osed cup)	рH	
CODE DESCRIPTION (ht ~ Unr2n-1)   FC-120 R(SO_3^*NH_4^* (n ~ 10))   FC-129 R(SO_2N(C2H_3)(C+12O_2^*K^*;n ~ 8))   FC-135 R(SO_2N(C2H_3)(C+12O_1^*(r + 3)))   FC-170 R(SO_2N(C2H_3)(C+12O_1^*(r + 3)))   FC-171 R(SO_2N(C2H_3)(C+12O_1^*(r + 4)))   FC-430 Fluoroaliphatic Pc-ymeric Esters   FC-431 Fluoroaliphatic Pc-ymeric Esters   FC-740 Fluoroaliphatic Po-ymeric Esters   *No.(tor specification putposes *No.(tor specification putposes		Anionic Anionic Cationic Nonionic Nonionic Nonionic Nonionic	25% 50% 80% 100% 50% 50%	: 0 : 3 1.2 1.3 1.4 1 1 1 0 1.0	10 30 400 150 7000 50 150	11 5: >300 >300 >20	88F (58C) 5F (46C) 3F (11C) DF (>148C) 0F (>148C) 00F (>93C) 8F (-8C) 02F (55C)	8.5-9.5 8-11 3-5** 6-8 6** 7** 7** NA	
TABLE 5. SOLUBILITY OF FLUOROSUR (GRAMS OF SURFACTANT/100	FACTA	NTS IN 8	OLVENT	6					
SOLVENT	FC-12	0 FC-12	9 FC-13	5 FC-170C	FC-171	FC-430	FC-431	FC-740	
Distilled Water Methyl Alcohol Ethyl Alcohol Ethyl Alcohol Ethylene Glycol Monobutyl Ether Dipropylene Glycol Monobutyl Ether Ethylene Glycol Monobutyl Ether Acetone Methyl Ethyl Ketone Niaz Lg-56 Triol Phenyl Glycidyl Ether Dibutyl Phthalate Dimethylformamide Polymeric Isocyanate Toluene Solvesso 100 Kerosene Heptane	<pre>&lt;1 0 10 10 10 10 10 10 10 10 10 10 10 10</pre>	x10 v v v v v v v v v v v v v v v v v v v	>10 >20 2 	-0.1 100 100 100 >20 >5 - - - <1 - - <1 - - <	-0.1 2-5 100 >20 - 20 - 20 - 20 - 20 - 20 - 20 - 2	>20 3 100 >10 100 200 1 0.5 1 >20 5 >20 5 >20 5 20 5 -10 -1 <1	<1 >10 100 >20 - >20 >100 >20 >100 >20 <1 >20 >20 >20 >20 >20 >20 - - - - - - - - - - - - -	<1 <1 <1 <1 <1 <1 <1 00 100 100	
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