

TECHNICAL INFORMATION

Chemical Division



3M BRAND FLUOROCHEMICAL SURFACTANTS

FC-95, FC-98, FC-128, FC-134, FX-161,
FC-170, FX-172

**Exhibit
1042**

State of Minnesota v. 3M Co.,
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CONTENTS

Introduction

Surfaces or Interfaces

Surface Tension

Surfactants

Fluorochemical Surfactants

Measurement of Surface Tension

Characteristics of 3M Brand Fluorochemical Surfactants

Solubility of 3M Brand Fluorochemical Surfactants

Handling and Use

Surface Properties

Introduction

Surface Tensions in Water

Surface Tensions in Acids

1. Hydrochloric Acid
2. Nitric Acid
3. Phosphoric Acid
4. Sulfuric Acid

Surface Tensions in Alkali

1. Potassium Hydroxide
2. Sodium Hydroxide

Surface Tensions in Other Media

Interfacial Tension

Emulsification

Foaming Power

Wetting Power

Applications of 3M Brand Fluorochemical Surfactants

Introduction

Guide to the Selection of 3M Brand Fluorochemical Surfactants

Cleaners

1. Alkaline Cleaners
2. Bottle Cleaners
3. Concrete Cleaners

Corrosion Inhibitors - Corrosion Resistant Films

1. Corrosion Inhibitors - General
2. Steel
3. Protective Coatings

Dips, Etches, and Strikes

1. Aluminum Bright Dip
2. Copper and Brass Bright Dips
3. Aluminum Acid Etch
4. Aluminum Base Etch
5. Magnesium Etches
6. Copper Strikes

Electrolytic Processes

1. Chrome Plating
2. Nickel Plating
3. Electrochemical Milling

Evaporation Inhibition

Organic Reactions

1. Hydrolysis
2. Sulfonation

Paper Pulping

CONTENTS (continued)

Pickling or Descaling

1. Steel
2. Stainless Steel
3. Spring Steel

Resins and Plastics

Solvents

Water Treatments

1. Open Cooling Water Systems
2. Closed Heating Systems

Waxes

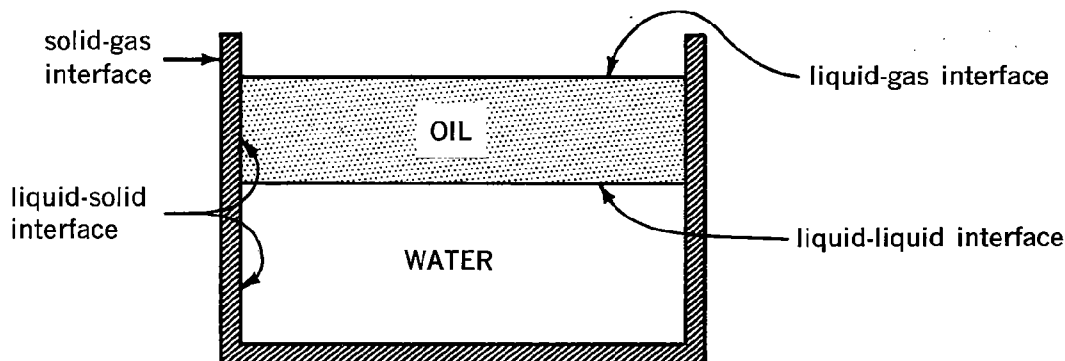
1. Alkaline Systems
2. "Lock and Key" Systems

Toxicity

Bibliography

TECHNICAL INFORMATIONINTRODUCTIONSurfaces or Interfaces

Oil and water do not mix, hence, there is a boundary between them. These boundaries, known as surfaces or interfaces, exist between liquids and liquids, liquids and solids, solids and solids, solids and gases, and liquids and gases.

Surface Tension

Liquids often behave as though there is an elastic skin stretched on their surface. A water glass, for example, can be filled to a point where the water level is above the rim of the glass, or a needle can be floated on the surface of the water. The strong "elastic membrane" or high surface tension of the water makes these effects possible. If you were to add a detergent to

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WARNING! Do not take internally. Avoid breathing dust. Wash thoroughly after handling.



- 3 -

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Surface Tension (continued)

the water, the glass could not be filled above the rim and the needle would not float. The elastic skin loses its strength; the water becomes wetter; its surface tension is reduced. Measurements of surface tension are, therefore, able to compare the effectiveness of compounds to concentrate at the surface and so effect the properties.

Surfactants

Any material capable of reducing the surface tension of a liquid is a surfactant, or surface active agent. In the illustration above, a detergent reduced the surface tension of water. Hydrocarbon detergents are excellent surfactants and are capable of reducing the surface tension of water from 72 dynes/cm. to 30-35 dynes/cm. These materials are commonly used in many processes such as washing clothes and dishes, emulsifying components of paint, industrial cleaning and etching, textile dyeing, and countless other applications.

Fluorochemical Surfactants

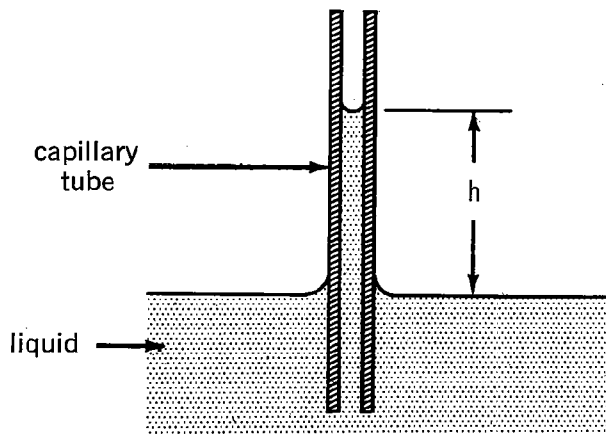
A fluorochemical surfactant contains a completely fluorinated tail and solubilizing group. These compounds are capable of reducing the surface tension of water from 72 dynes/cm. to 15-20 dynes/cm. Like the hydrocarbon surfactants, they are also active at all interfaces.

The difference between hydrocarbon and fluorochemical surfactants is further illustrated by concentration requirements. Minimum surface tension reduction of hydrocarbon surfactants (30-35 dynes/cm.) is generally achieved at concentrations of 0.1-1% by weight; while fluorochemical surfactants can achieve a minimum surface tension (15-20 dynes/cm.) at approximately 0.01% by weight (100 parts per million).

Determination of Surface Tension

Surface tensions can be measured in any one of a number of ways.

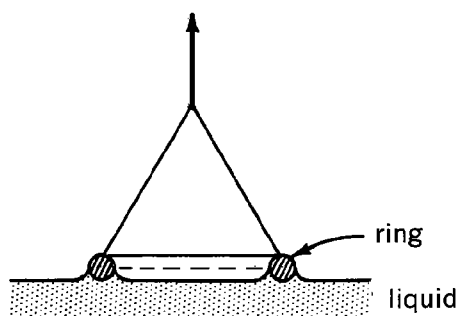
Capillary Rise: This method is the oldest, going back to Leonardo de Vinci. When a vertical capillary is immersed in a liquid which wets it, the liquid rises to a height, h , which is inversely proportional to the surface tension.



Determination of Surface Tension (continued)

The internal radius of the capillary tube, density of the liquid, and the acceleration due to gravity must also be known. Exact measurements of height and radius of the capillary are extremely difficult; hence, accuracy of the method is limited.

2. Drop Weight: The weight of a drop which falls from a capillary tube is proportional to the surface tension of the liquid and the radius of the capillary. Instruments currently available, called drop-counters and stalagmometers, are based on this principle. A serious disadvantage of the method exists, however, in that drops must be formed very slowly, only one in every several minutes. This measurement is neither accurate nor rapid.
3. Rupture of the Surface. "Tensiometer": Probably the fastest and most reliable method of surface tension measurement is the pull-ring method by duNouy. The procedure measures the "tension" or pull required to cause a ring to break free from the liquid surface. The tensile force is proportional to the surface tension.



The accuracy of the duNouy Tensiometer is especially great if liquids having similar properties are compared. It is also a fast procedure, capable of measuring surface tension of rapidly aging systems. Platinum rings are used; hence, clean-up between measurements is simplified over the capillary methods.

Additional information on surface tension measurements is found in the bibliography references (1, 2). The extremely low surface energy of the fluorocarbon tail is also discussed (3, 4).

CHARACTERISTICS OF 3M BRAND FLUOROCHEMICAL SURFACTANTS

The main features which distinguish these materials from conventional surfactants are as follows:

1. Stability
 - a. Chemical - Several are stable in 90% H₂O₂, anhydrous hydrazine, hot concentrated mineral acids, and alkalis.
 - b. Thermal - Certain members of this family are stable up to 750°F.
 - c. Biological - Some are completely resistant to biological attack.
2. Surface Activity
 - a. Aqueous Systems - Capable of surface tension reduction, 10-15 dynes/cm. lower than conventional surfactants.
 - b. Organic Systems - Many 3M surfactants are active in organic systems, causing reductions in the surface tensions of organic solvents.
 - c. Wetting - Wetting of materials can be greatly improved. Or, a variety of substrates can be made hydrophobic and/or oleophobic.
 - d. Foams - Stable, long-lasting foams can be produced in media which would be destructive to conventional surface active agents. Low foaming materials are also available.
3. Efficiency
 - a. Economical - Effective at extremely low concentrations, frequently at 50-100 parts per million or less.

SOLUBILITY OF FLUOROCARBON SURFACTANTS

<u>SOLVENT</u>	<u>SOLUBILITY</u> Grams Surfactant per 1000 Grams of Solvent, 25°C.						
	<u>FC-95</u>	<u>FC-98</u>	<u>FC-128</u>	<u>FC-134</u>	<u>FX-161</u>	<u>FC-170</u>	<u>FX-172</u>
Acetone	100	20	2	> 10	> 1000	600	1000
Benzene	0.8	0.2	0.2	0.6	2	500	1
Carbon Tetra- chloride	0.04	0.04	0.1	Nil	0.8	470	2
Ethyl Alcohol	2	20	10	100	80	> 1000	> 1000
Heptane	0.03	0.09	0.03	Nil	0.7	7	1
Isopropyl Alcohol	3	30	8	10	> 1000	> 1000	> 1000
Isopropyl Ether	0.1	0.3	0.2	0.04	20	250	15
Methyl Alcohol	60	40	60	80	70	> 1000	> 1000
Perchloro- ethylene	0.07	0.09	0.2	0.04	0.7	690	100
Toluene	1	0.2	0.1	0.1	1	550	10
Water	2	10	200 (gel)	> 5 (gel)	10	> 300 (gel)	> 500 (Foam)

Procedure Used Above: Saturated surfactant solutions were equilibrated and filtered. Solubilities were determined after evaporation of the solvent.

SOLUBILITIES IN ACIDS AND ALKALI

	<u>FC-95</u>	<u>FC-98</u>	<u>FX-161</u>
Hydrochloric acid, 12½%	> 1	< 10	< 0.01
Hydrochloric acid, 37%	0.1		
Nitric acid, 12½%	> 1	< 20	< 0.01
Nitric acid, 70%	> 5		
Phosphoric acid, 12½%	> 1		
Phosphoric acid, 85%	> 1		
Sulfuric acid, 12½%	10	< 10	< 0.01
Sulfuric acid, 97%	0.5		
Potassium hydroxide, 20%	1		

HANDLING AND USE

The solubilities of the 3M Brand Fluorochemical Surfactants in aqueous and organic media are usually lower than those of conventional hydrocarbon surfactants. Although the solubility limits of a given 3M surfactant in water may be 0.1% or less, this is not necessarily restrictive of its capacity to function effectively. However, the surfactant must have some solubility in a system if it is to be effective. Surface tension should be checked when solubility is in question, to determine whether or not the material is actually present in adequate levels to affect surface properties of the system significantly. Examination for color change and foaming can also be used as guides to indicate adequate solubility. In the case of surfactant use as a primary emulsifier, addition levels higher than 0.1% are usually required. Their use as secondary emulsifiers or stabilizers may not require use levels greater than this.

Where solubilities are not sufficient to achieve results in a particular media, it is recommended that the use of cosolvents be investigated. In many cases this will mean the addition of only a few percent of a cosolvent (or cosolvents) to form a binary or ternary system. For example, the addition of 5% acetone or isopropanol greatly increases the solubility of many fluorochemical surfactants in water. Similar examples occur with organic systems.

Because of low solubilities, 3M Brand Surfactants may be slow to dissolve. The use of heat will greatly increase solution rates and is recommended whenever possible. In some cases, pre-dissolving the surfactant in a small amount of a compatible solvent in which its solubility is large will greatly facilitate its solution. In such cases, very little of the pre-solvent will be needed; in fact, simple wetting out of a solid surfactant will often serve to increase its rate and degree of solution. It should be emphasized that:

Wherever possible, the surfactant should be added to a liquid system in a compatible liquid form. (This will insure that all of the surfactant which has been added is being utilized.)

The following is intended as a guide to helpful cosolvents for various 3M Brand Fluorochemical Surfactants.

<u>SURFACTANT</u>	<u>COSOLVENTS FOR WATER SOLUTIONS</u>	<u>COSOLVENTS FOR ORGANIC SOLUTIONS</u>
FC-95	Acetone or	50:50 CCl ₄ :methanol or
FC-98	Methanol	50:50 acetone:isopropanol
FC-128	Acetone or Isopropanol	Same as above
FC-134	Acetone Methyl cellosolve or Dimethyl formamide	Carbon tetrachloride
FX-161	Acetone or Isopropanol	Same as FC-95
FC-170	None required	Toluene Alcohol
FX-172	Acetone or Isopropanol	Acetone Isopropanol

SURFACE PROPERTIES

Surface tension measurements are included to show the effect of 3M Brand Fluorochemical Surfactants in water, various acids, alkalis, and other media.

Generally speaking, lowered surface tension values imply better wetting properties of the surfactant solution. This is true for many of them in many media. However, some of these surfactants are very capable of preferential absorption on many surfaces which, in effect, would decrease the wettability of that surfactant solution to that particular surface. An example of this diverse effect is the use of Fluorochemical Surfactants in hydrochloric acid. FC-95 will cause a great increase in the rate of attack of HCl on aluminum, while FX-161 can actually stop the corrosion of aluminum by formation of a tenacious monomolecular corrosion-resistant barrier film on the aluminum. It should be emphasized that the surfactant effects just described are very selective. The solvent, surfactant, and substrate are dependent upon one another. Our laboratories will be pleased to assist in the selection of the proper fluorochemical surfactant for problem applications upon receipt of complete information on the system and the effects desired.

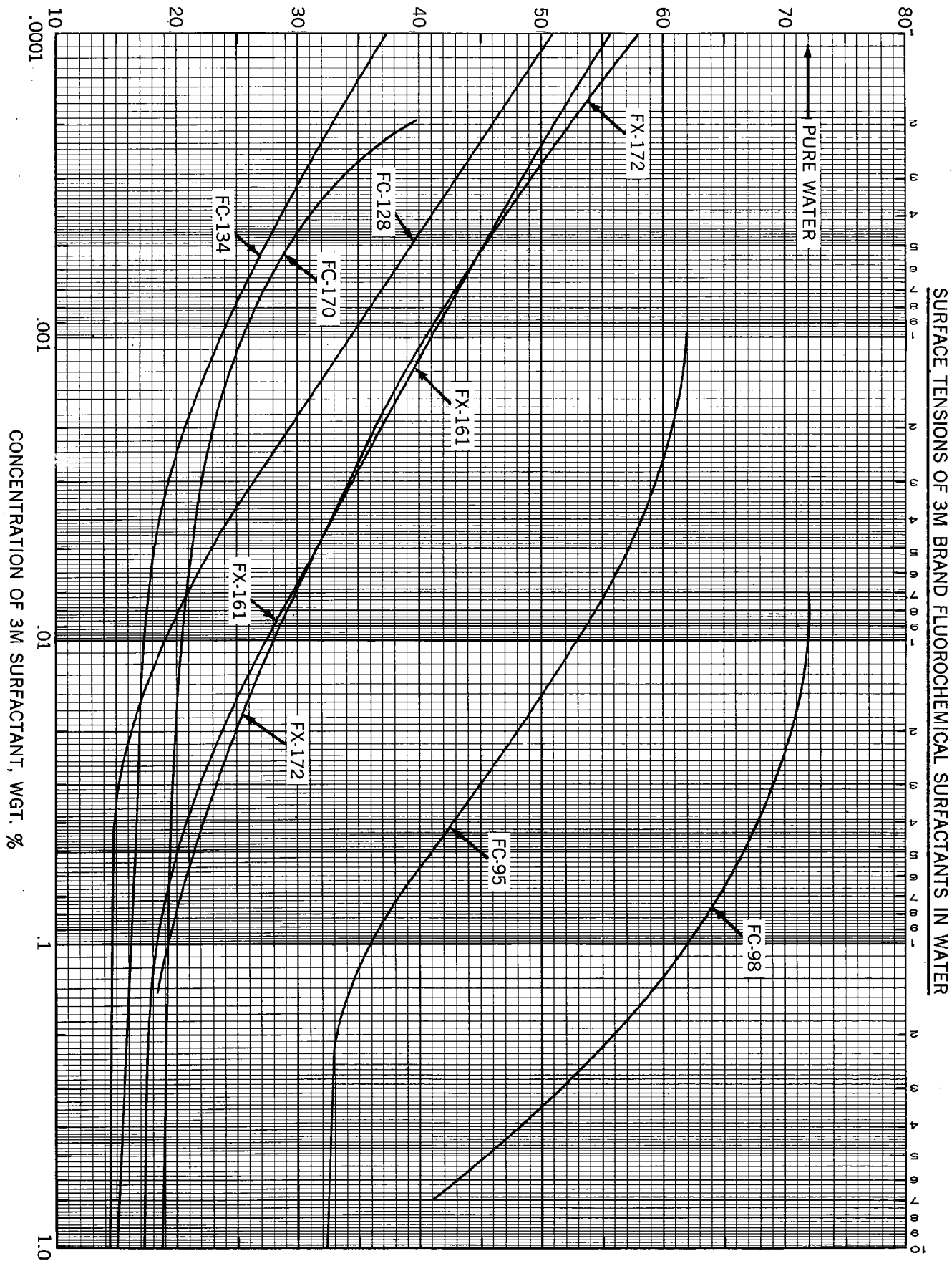
Unless stated to the contrary, all surface tension data presented were obtained with a duNouy tensiometer on solutions which had aged 16-24 hours prior to measurement. (See introduction)

SURFACE TENSIONS IN WATER

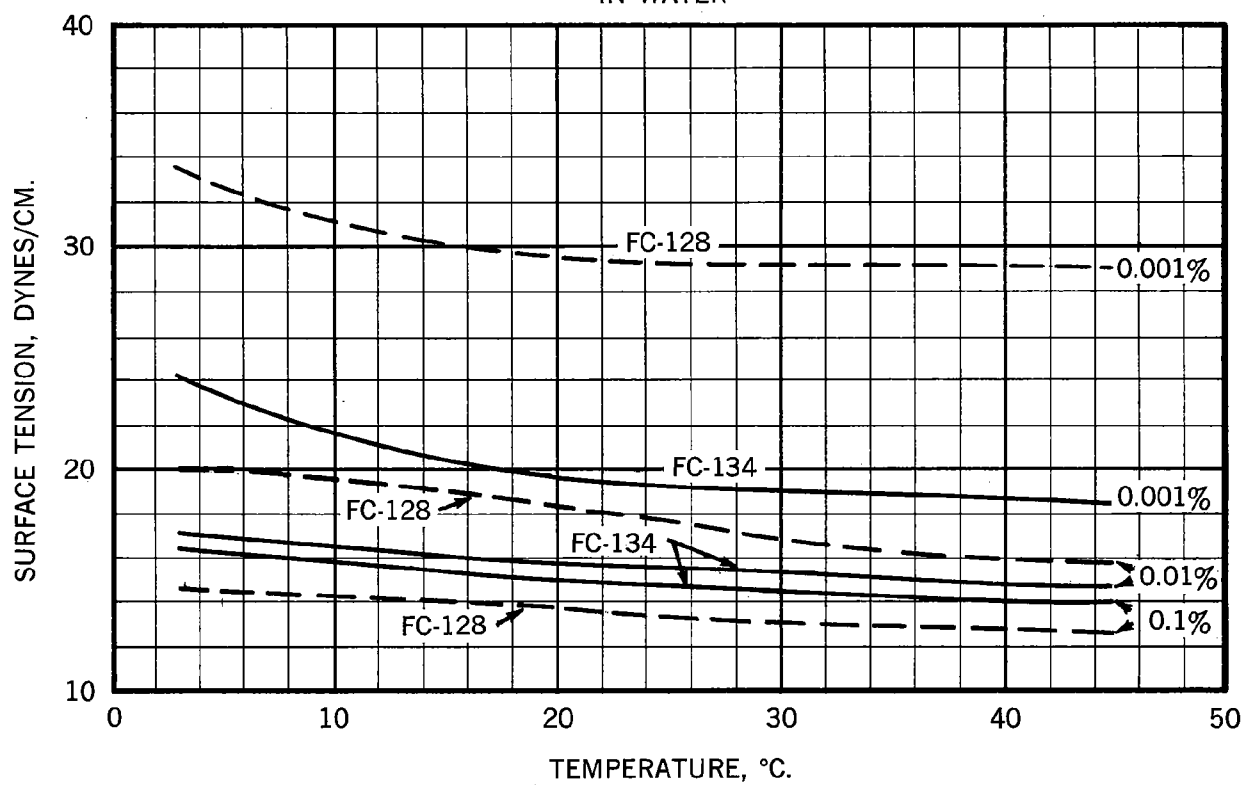
Figure 1 compares surface tension vs. concentration of 3M Brand Fluorochemical Surfactants in water. It should be noted that extremely low concentrations of FC-134 and FC-170 give remarkably low surface tensions in water. For example, 0.001% (parts per million) FC-134 reduces the surface tension of water from about 72 dynes/centimeter to about 24 dynes/cm.

Figure 2 represents the effect of temperature on the surface tensions of FC-128 and FC-134 solutions; each at concentrations of 0.1, 0.01, and 0.001 (1,000, 100, and 10 ppm respectively).

SURFACE TENSION, 25°C., DYNES/CM.



SURFACE TENSION vs. TEMPERATURE OF FC-128, FC-134
IN WATER



SURFACE TENSIONS IN ACIDS

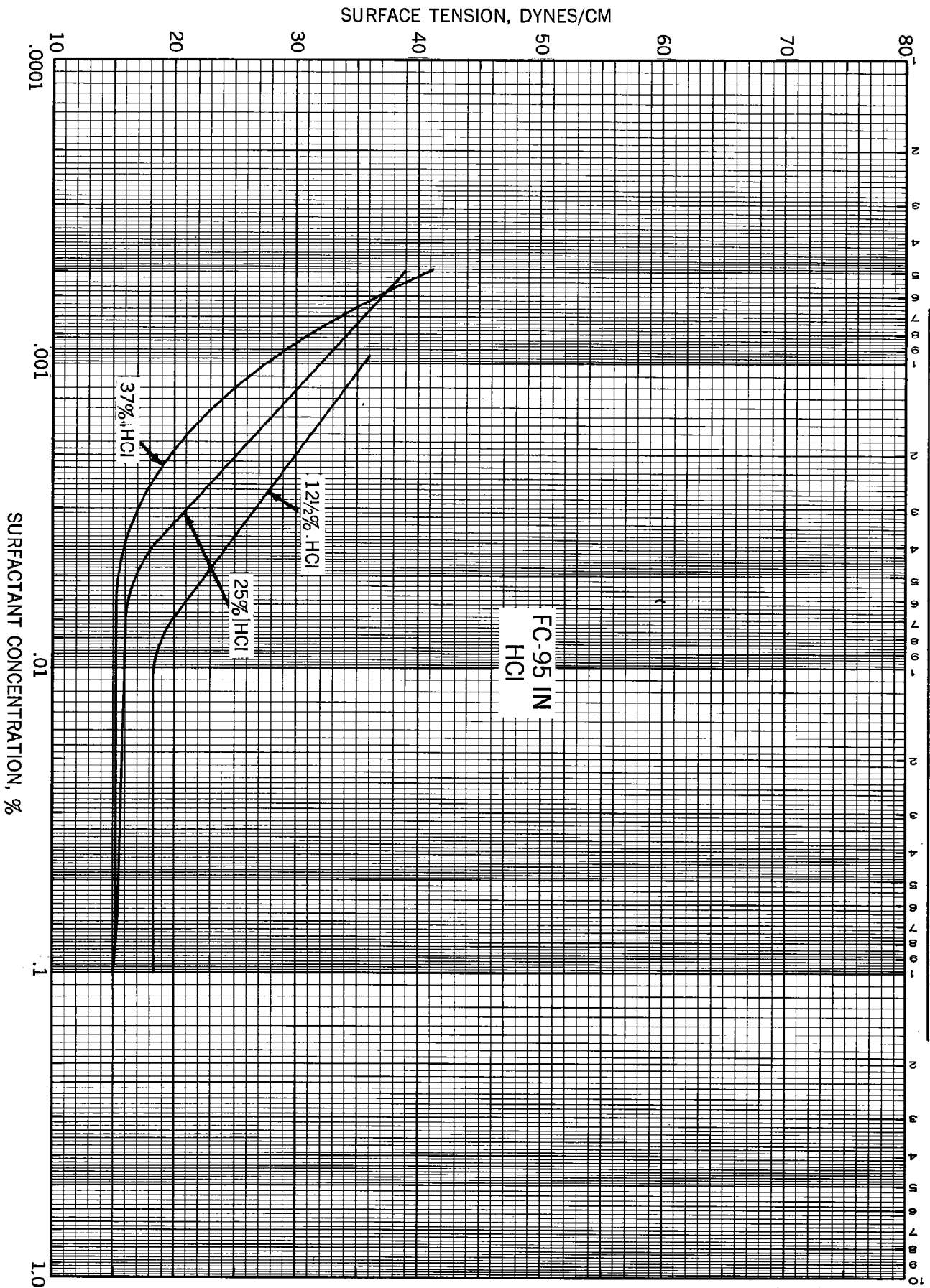
The stability of certain 3M Brand Fluorochemical Surfactants to strong mineral acids provides a unique means of reducing surface tensions of these highly corrosive chemicals. Certain of the fluorochemical surfactants are extremely stable in these acids even at elevated temperatures, and are often the only materials which provide surface activity in these media.

The effectiveness of materials such as FC-95 and FC-98 in reducing surface tension of acidic media is in marked contrast to their effect in water. The importance of solution pH is, therefore, not to be overlooked. Both solubility and activity are dependent on pH, the presence of other dissolved salts, etc.

1. Hydrochloric Acid

Curves for FC-95 in 12½%, 25%, and 37% hydrochloric acid are found in Figure 3. Note that minimum surface tension is attained at from 50 to 100 ppm (.005-0.01%) FC-95.

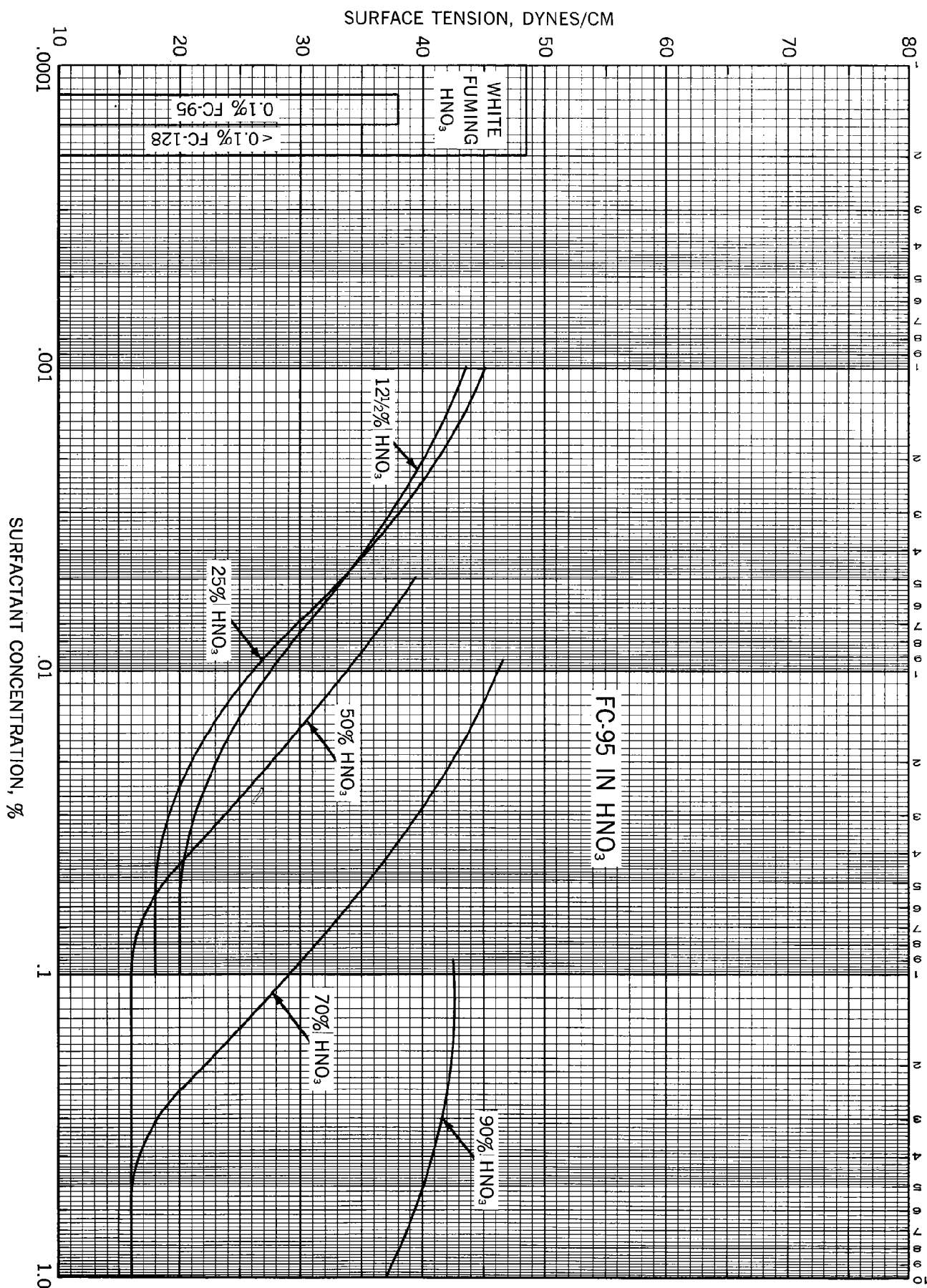
SURFACE TENSIONS OF FLUOROCHEMICAL SURFACTANTS IN HYDROCHLORIC ACID



2. Nitric Acid

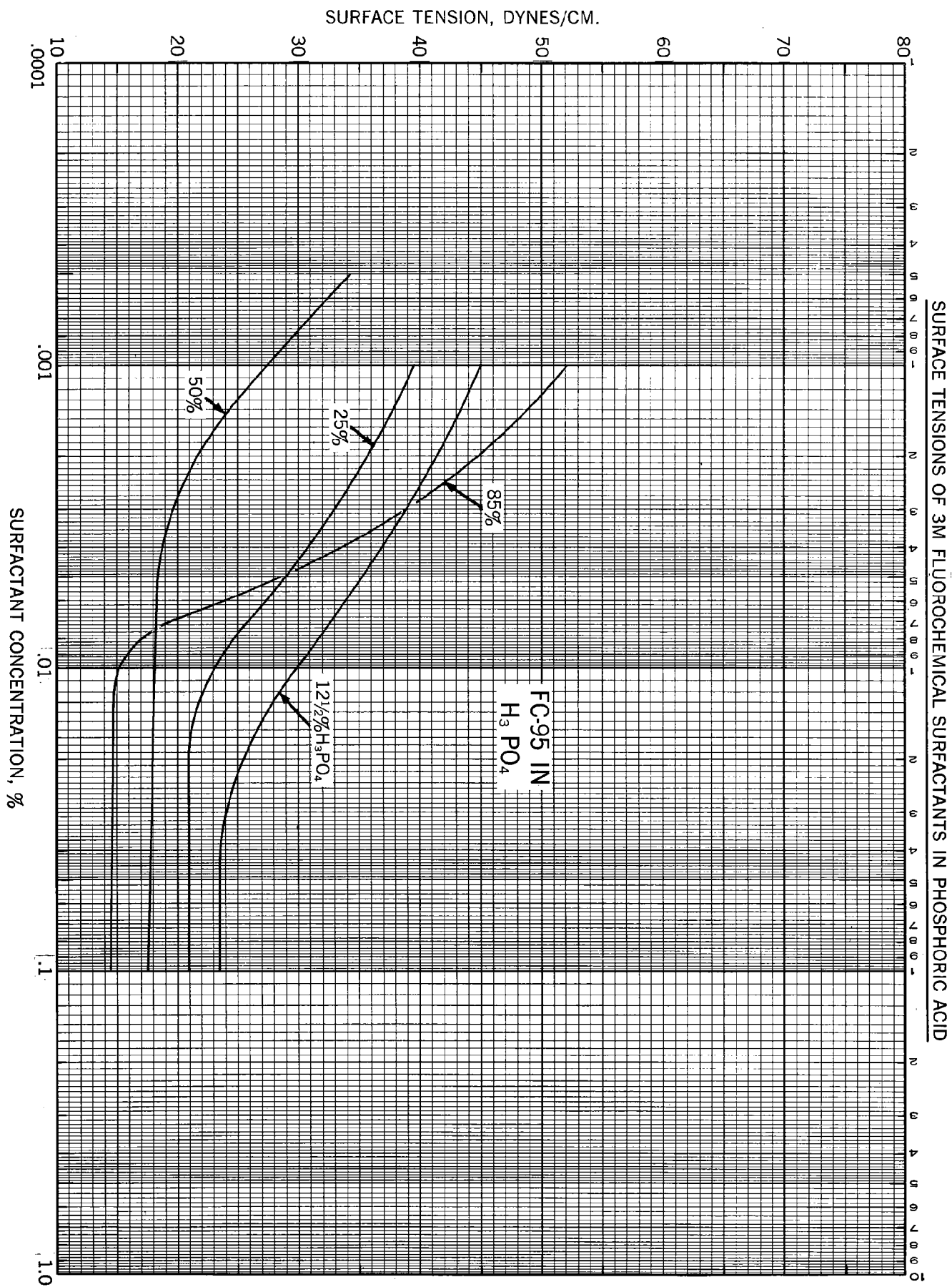
Figure 4 presents surface tension vs. concentration curves for FC-95 in $12\frac{1}{2}$, 25, 50, 70, and 90% HNO_3 . Bar charts are included showing the effect of FC-95 and FC-128 in white fuming nitric acid. The area at the left of the bar chart indicates the surface tension of the pure acid.

SURFACE TENSIONS OF FLUORO-CHEMICAL SURFACTANTS IN NITRIC ACID



3. Phosphoric Acid

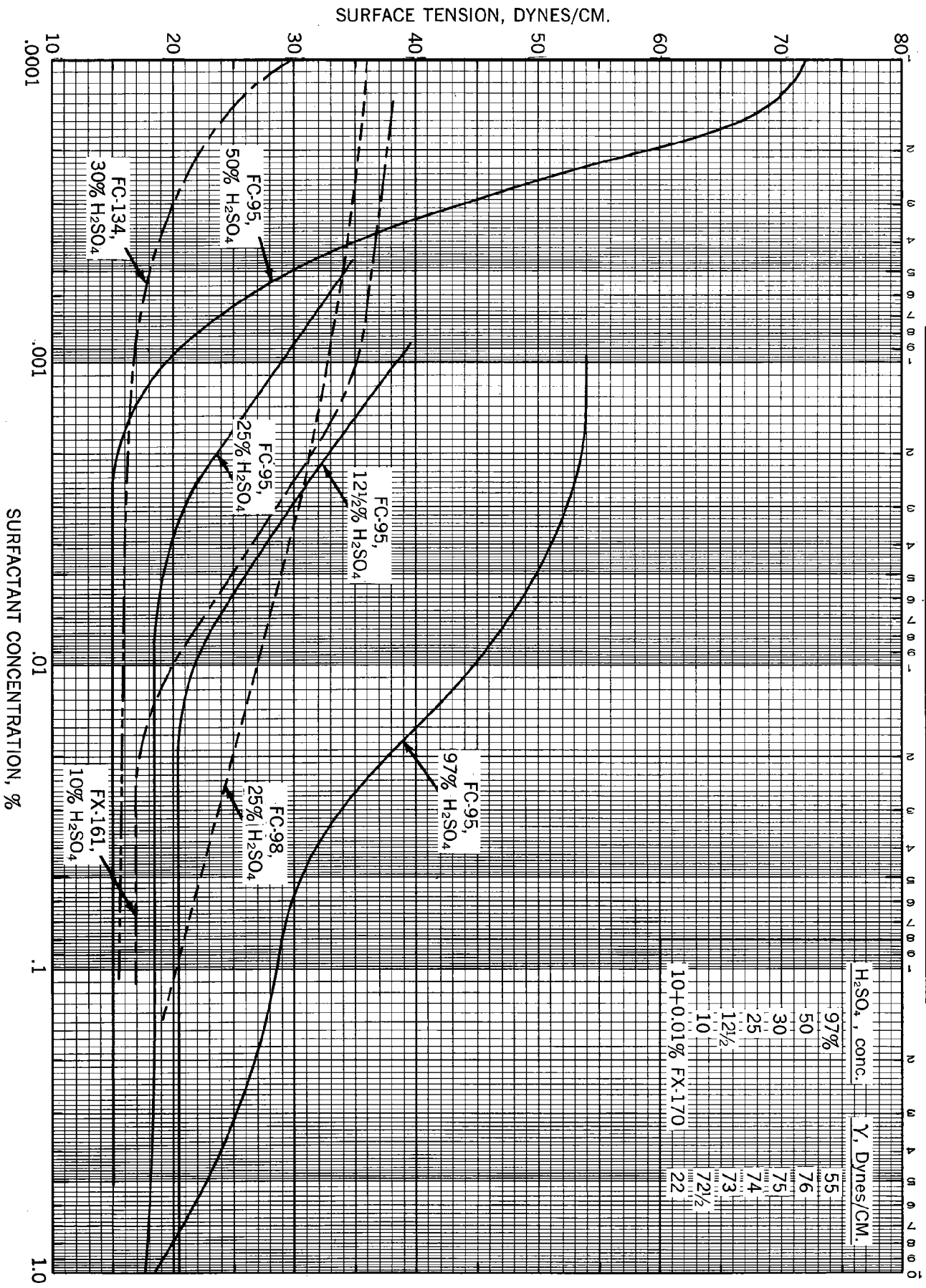
Curves indicating the effect of FC-95 in 12½, 25, 50, and 85% H₃PO₄ are given in Figure 5. Note that minimum surface tensions are achieved at concentrations of 50-500 ppm (0.005-0.05%) FC-95.



4. Sulfuric Acid

Many 3M Brand Fluorochemical Surfactants show excellent surface activity in sulfuric acid as shown in Figure 6. Curves of surface tension vs. concentration are given for FC-95 in 12½, 25, 50, and 97% H₂SO₄, for FC-98 in 25% H₂SO₄, for FC-134 in 30% H₂SO₄, and for FX-161 in 10% H₂SO₄. By way of comparison, the surface tensions of the pure sulfuric acid solutions are given in the upper right-hand corner.

SURFACE TENSIONS OF FLUOROCHEMICAL SURFACTANTS IN SULFURIC ACID



In acid media it is often possible to observe an even lower surface tension with time. The following table illustrates this effect.

FC-134 in 30% Sulfuric Acid vs. Time

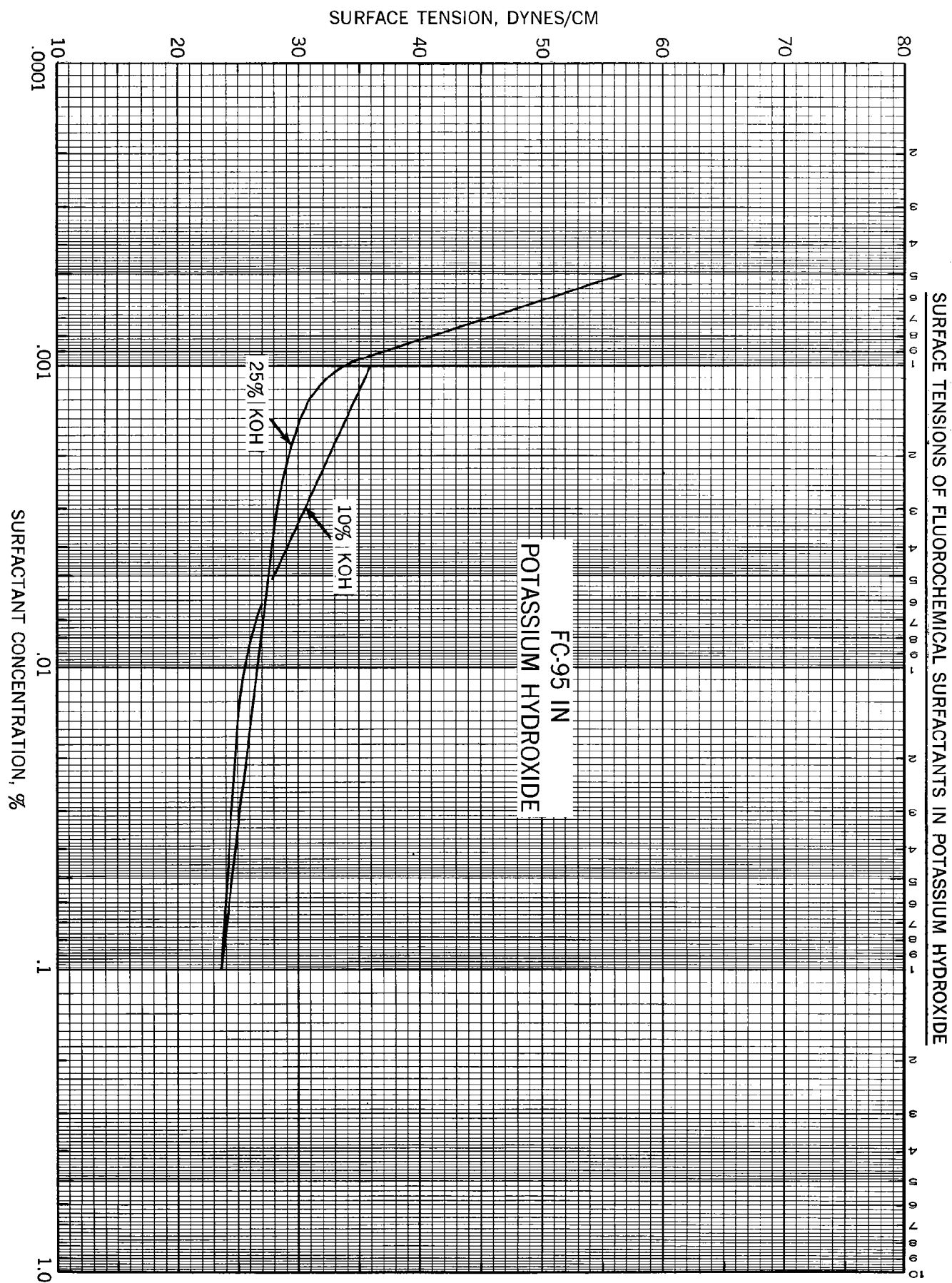
<u>Concentration of FC-134%</u>	<u>0.1</u>	<u>0.01</u>	<u>0.001</u>	<u>0.0001</u>
Freshly mixed	15.2	16.4	24.4	71.9
After 48 hrs. standing	15.5	16.0	16.8	29.4
After 48 hrs. standing plus heating 16 hrs. @78°C.		14.1		24.5

SURFACE TENSIONS IN ALKALIS

3M Brand Fluorochemical Surfactants show excellent surface tension reduction at low concentrations in alkaline systems.

1. Potassium Hydroxide

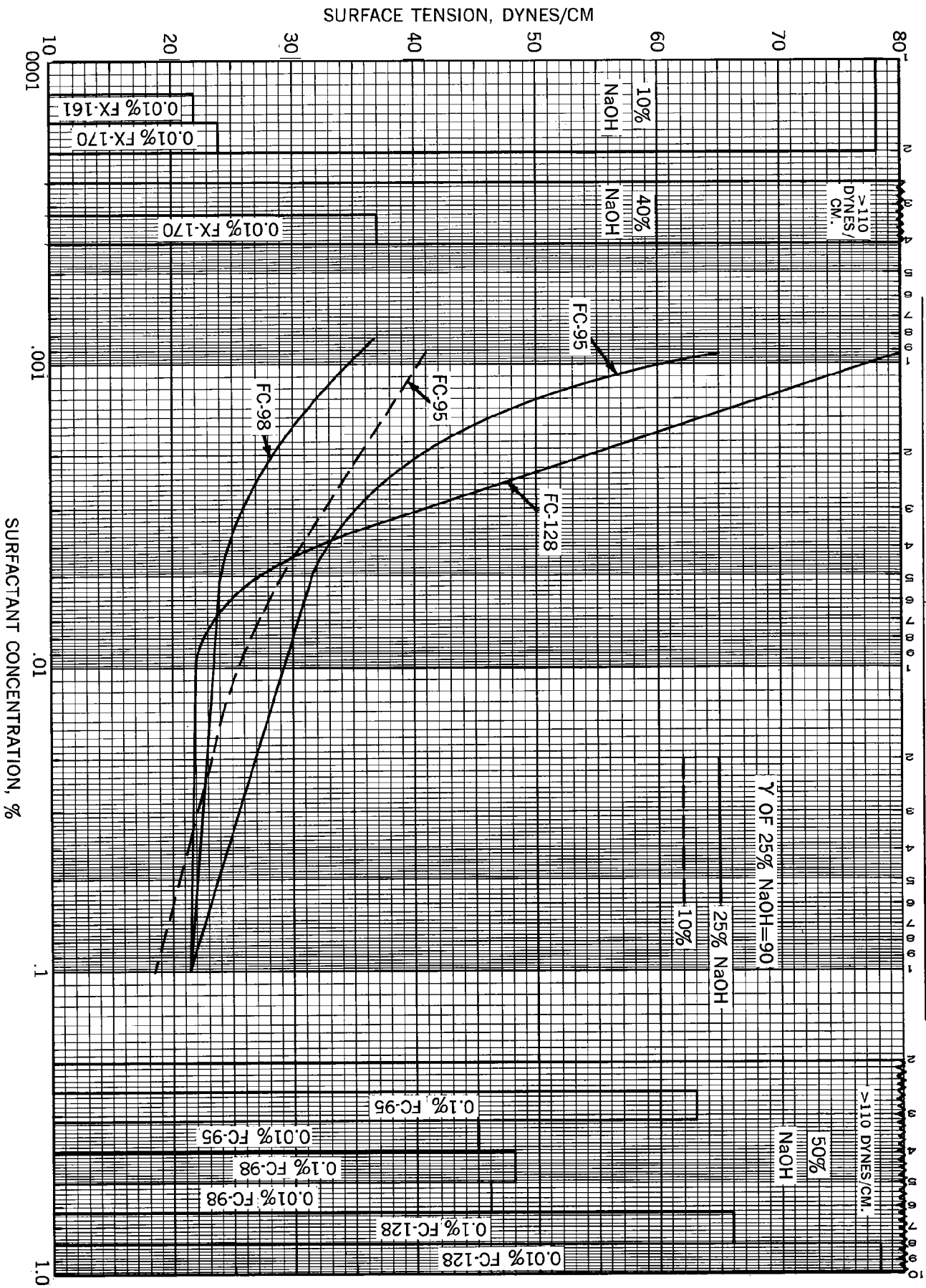
Curves for the effect of FC-95 in 10 and 25% KOH are given in Figure 7.



2. Sodium Hydroxide

Surface tension vs. concentration curves are presented in Figure 8 for FC-95 in 10 and 25% NaOH and for FC-98 and FC-128 in 25% NaOH. Bar charts illustrate the effect of other surfactants in 10, 40 and 50% NaOH. The bars at the left indicate the surface tension of the solution without surfactant.

SURFACE TENSIONS OF FLUOROCHEMICAL SURFACTANTS IN SODIUM HYDROXIDE



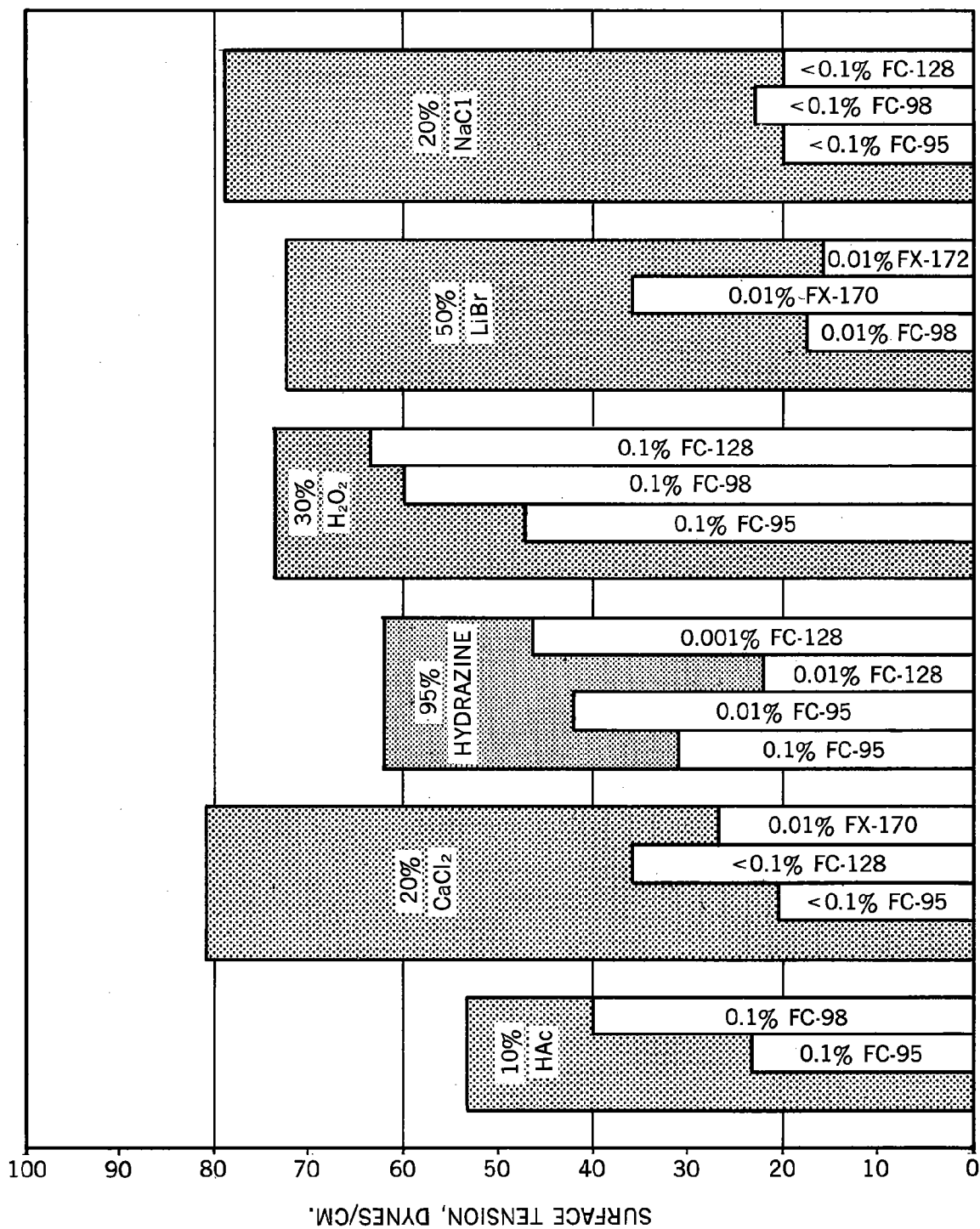
SURFACE TENSIONS IN OTHER MEDIA

The following bar chart, Figure 9 presents data on surface tensions of a variety of media containing fluorochemical surfactants:

1. 10% Acetic acid
2. 20% Calcium chloride
3. 95% Hydrazine
4. 30% Hydrogen Peroxide (at 18°C.)
5. 50% Lithium Bromide
6. 20% Sodium Chloride

Effectiveness and stability in such rigorous media as hydrazine and hydrogen peroxide is an important characteristic of these versatile surfactants.

SURFACE TENSIONS IN OTHER MEDIA



SURFACE TENSION REDUCTION IN DETERGENTS

FC-134 effectively reduces the surface tension of a commercial dishwashing compound (0.8% in water at 145°F.) as noted below:

<u>FC-134 CONCENTRATION</u> %	<u>SURFACE TENSION,</u> dynes/cm.
0 (control)	30.3
0.002	21.0
0.003	16.2
0.005	14.2

A comparison of these values with points on the curve of FC-134 in water, Figure 1, indicates a slight synergistic effect between the two compounds.

INTERFACIAL TENSION

The interfacial tensions between acids and organic liquids can be greatly reduced with FC-95. For example, the interfacial tension between concentrated hydrochloric acid and an organic ester, tributyl aconitate, was lowered from 12.6 to 1.8 dynes/cm by the addition of 0.5% FC-95 to the acid phase. Figure 10 illustrates the effect of FC-95 on the interfacial tension between n-decane and dilute sulfuric acid solutions of various strengths:

FIGURE 10

INTERFACIAL TENSION OF DECANE-DILUTE SULFURIC ACID
SOLUTIONS CONTAINING FC-95

MOLAR CONCENTRATION OF SULFURIC ACID SOLUTION

EMULSIFICATION

Fluorochemical surfactants are effective emulsifiers. However, it is usually necessary to use concentrations equal to those required for hydrocarbon surfactants which often imposes an economic restriction on their use. Those applications which are destructive to conventional surfactants by heat or chemical attack are excellent areas for the use of the fluorochemicals as emulsifiers.

Synergistic effects are often encountered when fluorochemical surfactants are used in addition to conventional hydrocarbon emulsifier blends. Effectiveness at considerably lower total surfactant concentration is often realized.

Many vinyl polymers have been prepared by emulsion polymerization utilizing fluorochemical surfactants as the emulsifiers (see U. S. Patent 2,559,752). It has been demonstrated that significantly lower emulsifier concentrations may be used when fluorocarbons are used instead of hydrocarbon emulsifiers.

FC-128 and FC-170 are used to advantage for emulsifying liquids of low surface energy (silicones and fluorocarbons). An homogenizer is generally required.

FX-172 is an excellent stabilizer for latexes.

In applications where wetting is required, but where emulsification is not desired, fluorochemical surfactants should receive first consideration. Here, the normal, very low concentrations are used to provide excellent wetting with a low degree of emulsification.

FC-170 is also used to break certain emulsions.

FOAMING POWER IN WATER

(Ross-Miles Test, ASTM Method D 1173-53).

SURFACTANT	CONCENTRATION, %	TEMPERATURE, °C	FOAM HEIGHT, mm.	
			Immediate	After 5 Min.
FC-95	0.5	25	126	65
	0.5	50	169	97
	0.1	25	10	4
	0.1	50	103	17
FC-128	0.5	25	213	207
	0.5	50	259	233
	0.1	25	188	185
	0.1	50	232	210
	0.01	25	12	6
	0.01	50	15	7
FC-134	0.5	25	164	164
	0.5	50	232	222
	0.1	25	87	86
	0.1	50	159	149
	0.01	25	9	9
	0.01	50	14	12

FC-134 forms remarkably stable foams which, in some cases, will last for several hours. FC-95 gives foams especially stable in basic media. FC-95 and FC-98 give stable foams in acids. Foams in certain organic solvents can be formed by FC-134. FX-172 is excellent in strong acids (producing very stable "dry" foams) and in neutral aqueous media.

Although in many cases the foams produced by fluorochemical surfactants do not appear as good as foams produced by conventional surfactants, they have a demonstrated stability to heat and chemicals which makes them invaluable in these applications. Users of fluorochemical surfactants in foams have noted that many "unhealthy" looking foams were outstandingly effective in their applications.

Defoaming of certain organic systems is possible through the use of FX-161 and FC-170.

FOAMING POWER IN OTHER MEDIA

Foams produced by many surfactants are sensitive to water hardness and pH of the solution. These conditions have been tested with FC-128 where it was found that FC-128 produces its maximum foam at a pH of about 10. As the pH decreases, the foam does also. At a pH of 7 or below, little or no foam is produced.

Hardness in water also reduces the foams in FC-128 solutions. This factor is easily overcome by the use of water softening or sequestering agents.

WETTING POWER IN WATER

(Draves-Clarkson Test - Reference: American Association of Textile Chemists and Colorists Technical Manual and Yearbook).

SURFACTANT	CONCENTRATION, %	TEMPERATURE, °C.	SINKING TIME sec.
FC-95	0.1	25	over 300
	0.1	50	24
	0.1	70	35
FC-128	0.1	25	52
	0.1	50	13
	0.1	70	7
	0.05	25	223
	0.05	50	30
	0.05	70	19
FC-134	0.05	25	over 300
	0.05	70	25

FX-172 and FC-170 also show excellent wetting power. FX-172 is superior to FC-128 and FC-134 and considerably better than FX-161 and FC-170 in the wetting of fabrics at the 0.05-0.1% level.

APPLICATIONS OF 3M BRAND FLUORO-CHEMICAL SURFACTANTS

New uses for this class of industrial surfactants are continually being found. Examples of their diverse applications are presented below. These commercial products will continue to find additional problems which they can solve effectively and economically. In this respect they are augmented by a growing list of experimental laboratory fluorochemical surfactants whose structures are specifically designed for an even wider area of consumer applications. A request to our laboratories with full particulars as to the system involved and effects desired will result in recommendations of the experimental or production fluorochemical surfactants most likely suited to your application.

The highly specific nature of these materials makes any generalizations regarding their use extremely difficult. The "Guide to the Use of 3M Brand Fluorochemical Surfactants" on the following page lists the most important properties of each commercial product. The major outstanding characteristic of each product is underlined for emphasis.

It should be added that in comparative evaluations of these materials, it is frequently observed that one surfactant performs best in one test while another is definitely superior in a different effect. It is then very advisable to evaluate surfactant blends. These blends provide the major effects required and, synergistically, can often show performance vs. concentration characteristics superior to either surfactant alone. These effects are available with blends of fluorochemical surfactants as well as with hydrocarbon/fluorochemical surfactant blends.

GUIDE TO THE SELECTION OF 3M BRAND FLUORO-CHEMICAL SURFACTANTS

TYPE FORM & APPEARANCE	FC-95 anionic white, free flowing pd.	FC-98 anionic white, free flowing pd.	FC-128 anionic light tan, free flowing powder	FC-134 cationic brown, waxy solid	FX-161 anionic light colored solid	FC-170 nonionic amber liquid	FX-172 amphoteric viscous liq.
STABILITY to heat, chemicals others	390°C., excellent	350°C., excellent	good, good light sensitive	good, good	good, good	good, avoid strong bases	good, good
SUBSTANTIVE TO:	-----essentially nothing-----						
WETTING PENETRATION	fair	fair-good	good	poor	poor	very good	excellent
FOAMING	very good in acids & bases	good *	good in water, bases	good in water *	very low	good to poor	excellent in water, acids
METAL TREATMENTS; CORROSION	Descaling assist; increase acid attack on metals; cooling tower waters.	Aluminum bright dip	Alkaline cleaners - reduces smutting and decreases immersion time.	Inhibitor for aluminum in acid; pick- ling inhib. for SS in H ₂ SO ₄ ; acid copper strike.	Inhibitor for metals; reduces smut in bases.	Pickle in- hibitor in 15% H ₂ SO ₄ with FC-134	Fair descal- ing assist.
OTHER USES	Increases acid activity in hetero- geneous rea- ctions; imp- roves flow of powders.	Improves flow of powders; similar to FC-95, but more solu- ble.	Leaf wetting; remove buffing compounds; dis- perse solids; concrete anti- foam; floor waxes; excellent leveling; wets plastics without stress cracking; emulsion stabil- izer.	Improves flow of solid part- icles; floor waxes; good leveling.	Monomolecu- lar films; reduces ice adhesion on metals, oil and chemical barrier film	Wets plastics without stress crack- ing; fair antistat; extrusion aid; glass clean- ing; excell- ent surface tension depre- ssant; emulsion breaker,	Latex stabilizer; hydroscopic; evaporation inhibitor; excellent wetting agent.

* FC-98 and FC-134, 50/50, good antifoam in organics

CLEANERS

FC-98 possesses outstanding surface activity in highly alkaline systems. Concentrations as low as 0.002% (20 parts per million) in 25% caustic at 50°C. result in surface tensions of 30 dynes per cm. FC-95 and FC-128 are similarly effective.

1. ALKALINE CLEANERS

Commercial alkaline cleaners are highly selective and specific in their cleaning action. The high chemical stability and surface activity of the fluorochemical surfactants offer a new approach to improving the efficiency and broadening the selectivity range of these alkaline cleaners.

The following formulation is typical of an effective alkaline cleaner used to remove paint and other deposits from steel:

5% sodium hydroxide
0.01% FC-128
Temperature: 180°F.

The use of FC-128 in the cleaner requires half the immersion time and doubles its effective life.

An alkaline cleaning bath used on missile products uses 12 ppm FC-128. Cleaning speed is increased substantially at lower cost than the previous systems.

2. BOTTLE CLEANERS

These are used primarily where removal of aluminum labels is necessary. FC-98 at 5 ppm is superior to FC-95 primarily due to the requirement of supplying the cleaner in a concentrate form containing 50% NaOH + 5% gluconic acid. FC-95 is not sufficiently soluble to be used in this concentrate.

3. CONCRETE CLEANERS

Phosphoric-hydrochloric acid concrete cleaners show improved wetting of oily surfaces when FC-134 is used at levels of 25-100 ppm.

CORROSION INHIBITORS -
CORROSION RESISTANT FILMS

It has been found that 3M Brand Fluorochemical Surfactants act as corrosion inhibitors in various metal-acid systems. They may be used as additives to the acid media or they may be applied as a thin, protective film on the metal prior to contact with the acid. In some cases, they exhibit a pronounced synergistic effect with organic corrosion inhibitors.

1. CORROSION INHIBITORS - GENERAL

Examples of corrosion inhibiting power of fluorochemical surfactants as shown in following data:

<u>SYSTEM</u>	<u>CORROSION RATE, MILS PER YEAR</u>
304 Stainless steel in 10% hydrochloric acid at 150°F.	175
Same, with 0.01% FC-134	21
Aluminum in 2N (7%) hydrochloric acid at 75°F.	1410
Same, with 0.01 FC-134	190

From the above, the effectiveness of FC-134 in reducing corrosion of aluminum and stainless steel in hydrochloric acid is evident.

The importance of inhibitor concentration and its means of addition is illustrated in the following data:

<u>SYSTEM</u>	<u>CORROSION RATE, MILS PER YEAR</u>
1100 Aluminum in 10% hydrochloric acid at 75°F.	2320
Same, with 0.02% FX-161 *	710
Same, with 0.2% FX-161 *	204
Same, with 2.0% FX-161 **	264

2. STEEL

A very smooth etch is obtained when FC-95 is used in conjunction with thio-urea or ethyl mercaptan as a corrosion inhibitor for cold rolled steel in 5% H₂SO₄. A synergistic effect is observed with ethyl mercaptan and FC-95.

The following table lists corrosion rates, in mils per year, for the various systems.

* FX-161 added as 10% solution in acetone

** No cosolvent used. FX-161 was not all being utilized

2. STEEL (continued)

INHIBITION OF CORROSION ON COLD ROLLED STEEL BY 5% H₂SO₄ AT ROOM TEMPERATURE

Inhibitor	CORROSION RATE		MILS PER YEAR
	0-4 hrs.	0-146 hrs.	146-1035 hrs.
None	456		
0.5% FC-95	275		
0.011% Thiourea		8.8	15.6
0.011% Thiourea + 0.5% FC-95		8.1	12.5
0.093% Ethyl mercaptan		4.9	13.4
0.093% Ethyl mercaptan + 0.5% FC-95		5.0	1.1

3. PROTECTIVE COATINGS

Properly applied, FX-161 and FC-134 will improve the tarnish resistance of many metals exposed to corrosive environments as long as flushing conditions do not prevail. These films have oil and water repellency and resistance to fingerprinting. On sealed, anodized aluminum, increased salt spray resistance results, and 3% hydrochloric acid will not attack the surface. Similar effects have been noted on other metals including steel, brass, and copper. An effective procedure for preparation of these thin films is described below:

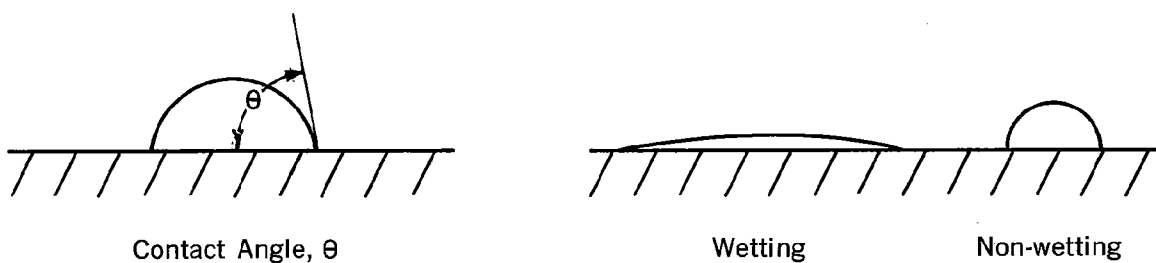
FX-161 on Aluminum

FX-161 is best applied to aluminum from acetone, alcohol, alcohol:water, or acetone:water solutions. Usually 0.5-2.0% solutions of FX-161 in isopropanol, ethanol, or acetone suffice to assure uniform coatings in single immersion dips of 10-30 seconds.

The aluminum to be dipped should first be cleaned and degreased completely (so that no water break is noted). Common degreasing solvents followed by a dip in dilute base and a complete flushing rinse will properly prepare the surface. Abrasive cleaning with "SCOTCHBRITE" following the degreasing is also recommended.

Slow removal of treated pieces from the bath will insure almost complete drainage. It is often possible to observe during withdrawal that the bath no longer "wets" the piece. Pieces should immediately be given a quick rinse in distilled water to remove any excess solution which, upon drying, might cause spotting. Heating the metal after treatment often improves the permanence and tenacity of the film.

The presence of the film is easily detected because of the auto-repellency of the bath (it no longer "wets" the metal) or by placing a drop of mineral oil on the surface. The drop should "bead up" showing a contact angle of 45° or more.



Note that where wetting occurs, the contact angle, θ , is very small. A drop exhibiting non-wetting has a large contact angle and there is no tendency for the drop to spread.

FC-134 is applied in the same manner from the same solvents or from acidified water. It provides good tarnish resistance for copper and brass even in the presence of high humidity and H_2S or SO_2 . Fingerprint and soiling resistance are also improved.

DIPS, ETCHES, AND STRIKES

Unusual effects are frequently observed when the fluorochemical surfactants are included in etches, strikes, stripping solutions, and dips utilized to achieve matte, or bright finishes, and the like. Such effects may include either accelerated reaction rate, inhibition of reaction, improved appearance and uniformity of attack, protection from staining after dipping, and development of water repellent surfaces.

1. ALUMINUM BRIGHT DIPS

FC-95 in a concentration of 0.005% (50 parts per million) causes an increase in the reaction rate of conventional phosphoric-nitric acid-based aluminum bright dips.

<u>TREATMENT</u>	<u>REACTION RATES</u> mg per sq. in. per 15 sec.
Aluminum in 90% phosphoric acid + 10% nitric acid at 170°F.	5.2
Same, with 0.005% (50 ppm) FC-95	11.7

Improved brightening is imparted. Due to the formation of a layer of foam at the bath surface, the mist and spray normally associated with these baths is eliminated.

FC-98 has a similar effect in these dips in the 25-50 ppm range. Increased reaction rate, improved brightening, and reduced drag-out losses occur.

FC-134 and FX-161 are useful in 10-15% hydrochloric acid bright dips for aluminum. Here, however, reaction rate is sharply reduced allowing very smooth, blue-bright finishes on aluminum alloys which would normally be spotty after such a dip. (See Corrosion Inhibitors.)

2. COPPER AND BRASS BRIGHT DIPS

FC-134 and FX-161 produce brighter finishes with reduced drag-out and improved stain resistance when incorporated into a 50% sulfuric 25% nitric, trace hydrochloric acid, copper bright dip solution. Superior fingerprint resistance and a lower degree of staining in nitrous oxide fumes is imparted when the final rinses contain 0.05-0.1% of the same surfactant, plus 10-20% alcohol.

Similar advantageous effects are obtained with brass:

<u>TREATMENT</u>	<u>REACTION RATE</u> mg per sq. in. per 30 sec.
Brass in 50% Sulfuric acid + 25% Nitric acid at 75°F.	7.8
Same, with 0.02% FX-161	9.5

2. COPPER AND BRASS BRIGHT DIPS (continued)

Drag out losses were reduced 25% and the brass was brighter after treatment with the bright dip containing 0.02% (200 ppm) FX-161.

3. ALUMINUM ACID ETCH

Smoother etches are obtained in a 15% hydrochloric acid system at 150-180°F. when 0.01% FC-134 or FX-161 is used. The reaction rate is reduced. (See Corrosion Inhibitors). The same quantities of FC-95 or FC-98 will sharply raise the rate of etch. If this is desired, FC-98 is preferred since FC-95 can cause blackening.

4. ALUMINUM BASE ETCH

FX-161 and FC-134 can be utilized in 2% sodium hydroxide to alter etching rates. For example, at 75°F 0.01% FC-134 will reduce the rate of attack about 10% while 0.02% FX-161 can increase this rate by 0-20%. Due to the speed of reaction, little or no increase in rate is observed during a short etch with FX-161. A longer immersion is required to show the 20% rate increase. The use of either surfactant will reduce surface tension of the bath which should result in reduced losses due to drag out.

5. MAGNESIUM ETCHES

In a 20% chromic acid or in an 8% nitric - 2% sulfuric acid etch. 50 ppm FC-95 sharply raises the rate of attack.

FC-95 and FC-98 are also effective in mist suppression, elimination of gray powder, and in producing a more desirable microscopically pebbled coating in chrome pickle for magnesium. This is a sodium dichromate, nitric acid solution at 70-90°F. FC-95 is suggested at the 0.02% level; FC-98 at 0.08%.

6. COPPER STRIKES

FC-134 and FX-161 are effective in a 3% copper sulfate, 3% sulfuric acid, 0.5% Carbowax 20M formulation. Used at the 0.01-0.1% level, these surfactants allow a several-fold increase in immersion time for the same deposition of copper. This results in a plating which is considerably more durable.

ELECTROLYTIC PROCESSES

1. CHROME PLATING (5, 6)

FC-95 and FC-98 possess extreme chemical resistance and surface activity in acid media. They are used to eliminate misting of decorative chrome plating baths, due to their ability to develop stable, fine foam blankets on top of the bath. In addition, drag out losses are reduced considerably and hazards to operating personnel are minimized. Decreased exhaust velocities and reductions in corrosion of exhaust systems is also attained.

These surfactants generally leave some pin holes in hard chrome plates but can be used to advantage in those applications where such an effect is tenable.

2. NICKEL PLATING

FX-161, 20 ppm, is useful as a non-foaming surfactant in the Watts type bright nickel plating bath. A significant reduction in surface tension of the bath is effected even at this low concentration.

3. ELECTROCHEMICAL MILLING

FC-128 has been shown effective in increasing the rate of metal removal in these applications at 10-100 ppm concentrations. Surface tension of a 25% sulfuric acid drilling electrolyte for a nickel alloy was reduced from 75 to 23 dynes/cm.

FX-161 at 10-100 ppm increases the rate of milling by a factor of about 2 without foaming. FC-128 causes foaming at these concentrations.

EVAPORATION INHIBITION

Reducing losses from evaporation is readily accomplished through the use of fluorochemical surfactants. The following illustrates the types of effects obtained in this application.

1. 1,1,1-Trichloroethane - Tests were conducted in open beakers, not in a draft, at room temperature

<u>SAMPLE</u>	<u>% SOLVENT RETENTION</u> <u>after 114 hours</u>
Control	19
0.01% FX-172	90
0.1% FX-172	92

2. Methylene Chloride - Tests were conducted in wide-mouth jars at room temperature in the draft of a laboratory hood. Approximating commercial practice, a layer of water was floated on the top of the solvent. The height of each phase remaining after 2 days is recorded.

	<u>Surfactant Used</u>			
	<u>None</u>	<u>FC-128</u>	<u>FC-134</u>	<u>FX-172</u>
<u>Water Phase</u>				
Original thickness, mm.	11.5	14.0	14.0	6.5
Retention, %	0	21	11	0
<u>Methylene Chloride Phase</u>				
Original thickness, mm	57.5	75.5	76.0	75.5
Retention, %	22	98.7	98.7	91.4

A sample with no water layer and no surfactant evaporated to dryness within six hours. FC-128 and FC-134 were used at 100 ppm in the water phase; FX-172 at 100 ppm in the methylene chloride phase.

3. JP-1 Aviation Kerosene - This jet fuel was evaluated at 140°F in a laboratory hood for 84 hours.

<u>SAMPLE</u>	<u>% FUEL RETENTION</u> <u>after 84 hours</u>
Control	52%
100 ppm FX-172	63%

Inhibition of solvent evaporation with fluorochemical surfactants is highly specific as to the solvent type. Our laboratories will be pleased to assist in selecting the best surfactant for a particular solvent.

PICKLING OR DESCALING OF STAINLESS STEEL

A 10% hydrochloric acid bath is effectively inhibited by 0.01%

FC-134. Corrosion is essentially stopped 30-60 seconds after immersion.

RESINS AND PLASTICS

The addition of Fluorochemical Surfactants to liquid resins reduces their surface tensions considerably. For example, the addition of 0.1% FC-134 to a liquid epoxy resin, reduced the surface tension to 34 dynes/cm. after 1 hour (from 48 dynes/cm. without surfactant). Such effects can be used to advantage to speed up the wetting of glass fibers or other fillers for the resin, to increase the rate of release of trapped air bubbles from these viscous resin systems, and to improve wetting of concrete, metal or other substrates to which they may be applied.

FC-170 in 0.1% concentration added to a phenolic resin (55% solids) from a 50:50 cellosolve:water solution, will reduce surface tension from 46.5 dynes/cm. to 24.2 dynes/cm. Improved speed and thoroughness of wetting asbestos or other fillers will result.

FC-128 and FC-170 may be used as wetting agents for water on polyethylene or other plastics. Unlike conventional surface active agents, they do not cause stress-cracking.

In many resin systems, water, oil, or soil resistance can be upgraded by the incorporation of small quantities of 3M Brand Fluorochemical Surfactants.

SOLVENTS

FC-128 and FX-161 speed up the rate of removal of epoxy resin based paints from magnesium and aluminum by methylene chloride paint strippers. Solvent evaporation may be reduced by certain fluorochemical surfactants. This effect is highly selective depending on the particular solvent involved since the solubility of the surfactant in the solvent is an extremely important factor. See the Evaporation Inhibition Section.

WATER TREATMENTS

1. Open Cooling Water Systems (8)

Laboratory studies indicated low corrosion rates would be obtained on mild steel in synthetic cooling water if FC-95 were used in conjunction with the noraml chromatic inhibitor. A summary of these 6-day test results of corrosion rate in mils per year follows:

CORROSION RATES OF MILD STEEL CORROSOMETER PROBES IN SYNTHETIC COOLING WATER

<u>INHIBITOR</u>	<u>CORROSION RATE, Mils Per Year</u>
None	60+
15 ppm Chromate*	7.5
25 ppm Chromate	4.6
40 ppm Chromate	3.3
5 ppm FC-95 + 15 ppm Chromate*	3.2
5 ppm FC-95 + 40 ppm Chromate	0.6
10 ppm FC-95 + 15 ppm Chromate*	2.9
10 ppm FC-95 + 25 ppm Chromate	0.4
10 ppm FC-95 + 40 ppm Chromate	0.4

*pH 4.0-4.5; all others pH 6.5-7.5

As a result of this laboratory work, this effect was verified in a forced draft cooling tower for 300 ton air conditioning condenser. The cooling system operated twelve hours a day and had a capacity of 3000 gallons. The circulating water temperature averaged 85 F., and the heat exchanger surface temperature was about 105°F. Circulation rate was 900 gpm, and blow-down averaged 4 gpm initially. After the first 49 days of the 115-day test, blowdown was discontinued to increase the scaling potential of the water.

Results were monitored with mild steel Corrosometer probes. With no inhibitor, a corrosion rate of 73 mpy was obtained. A level of 60 ppm chromate for filming the system, followed by 15 ppm chromate for film maintenance gave a 2.5 mpy corrosion rate. The addition of 10 ppm FC-95 to the 15 ppm chromate reduced the rate to 1.2 mpy in 3 weeks and to 0.9 mpy in 7 weeks. Duplication of the synergistic effect noted in the laboratory work was excellent.

2. Closed Heating System (8)

Another application of fluorochemical surfactants in the water treatment field has been in closed heating systems. Their use as a corrosion inhibitor in these systems evolved during an investigation of a somewhat unrelated problem, that of wear on pump seal rings in closed heating systems.

2. Closed Heating System (8) (continued)

The graphite seal rings were wearing to failure at a rapid rate in systems inhibited with 300 ppm chromate. It was believed that most of this wear was due to the evaporation of the high chromate water at the seal surface forming abrasive chromate crystals.

One of the systems in which a failure had taken place was charged with the combination 25 ppm chromate - 10 ppm FC-95. New graphite seal rings were measured by micrometer and installed in the pumps. Mild steel and Admiralty brass probes also were installed in the system. Results of this evaluation are shown below:

CORROSION AND SEAL WEAR EVALUATION

<u>PERIOD</u>	<u>INHIBITOR</u>	<u>CORROSION RATE, mpy</u>		<u>SEAL RING WEAR</u>
		<u>Steel</u>	<u>Admiralty</u>	<u>mils/month</u>
8.5 months	None	1.1	-	1.6
6 weeks	300 ppm Chromate	0.4	-	28.6
8 months	25 ppm chromate + 10 ppm FC-95	0.1	0.1	0.4

It is seen that besides maintaining or reducing the low corrosion rate, the FC-95 - low chromate combination inhibitor markedly reduced seal wear rates. It is possible that the surfactant is also acting as a surface lubricant on the seal rings.

WAXES

1. Alkaline Systems

Self-polishing floor waxes, based on polystyrene or acrylic emulsions are an excellent application for fluorochemical surfactants (7). These products require a high gloss, excellent durability to acid or neutral media, ease of application, stain and abrasion resistance, re-buffability, re-coatability, and ready removal with alkaline cleaners.

A typical formulation follows:

85 pbw - Emulsion polymer, 40% solids
5-10 pbw - Wax emulsion
5-10 pbw - Alkali soluble resin
2 pbw - Plasticizer
1 pbw - Fluorochemical surfactant, 1% solution

The emulsion polymer is the basic vehicle and can be acrylic, styrene, or a blend of the two. The wax emulsion gives buffability to the system. In the acrylic system, the alkali soluble resin acts as a leveling agent, while in the polystyrene system it acts as a carrier for the polymer and promotes ease of removal with alkaline cleaners. A plasticizer is required for the styrene systems - not for the acrylics. FC-128 or FC-134 are used to improve leveling, gloss, wetting power, and minimize streaking. At low concentrations (70 parts per million) no adverse effects on water resistance are noted.

2. "Lock and Key" Systems

The "Lock and Key" systems are those which employ resins which are insoluble in alkaline compounds, such as soaps and detergents, and which can be easily removed with acidic cleaners. The major advantages of these systems are:

- (1.) Scrubability with household cleaners without removing the finish.
- (2.) Higher gloss due to easy re-coatability, and
- (3.) Easy removal.

Formulation of these products is basically the same as the alkaline soluble systems, except that the resins are modified for acid solubility - alkali insolubility. Here, again, the fluorochemical surfactant does what normal surfactants could do in improving the compatibility and/or solubility of the various phases in each other, but at a level which will not cause sensitivity of the dried film to water or alkali

In applications of this type, it is recommended that both FC-128 and FC-134 be evaluated and compared.

TOXICITY

Toxicity classifications of 3M Brand Fluorochemical Surfactants range from slightly toxic to moderately toxic. Listed below are LD₅₀ values obtained by determination of acute oral dosage to adult rats and mice.

<u>SURFACTANT</u>	<u>LD₅₀ gm/Kg of Body Wgt.</u>	<u>CLASSIFICATION</u>
FC-95	0.45	moderately toxic
FC-98	0.18	moderately toxic
FC-128	0.75	slightly toxic
FC-134	0.5	slightly toxic
FX-161	6.2	slightly toxic
FC-170	3.2	slightly toxic
FX-172	2.0	slightly toxic

Due care should be exercised in handling these materials until further information is available on their physiological properties.

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