FACTORS AFFECTING THE SELECTION OF FOAMING AGENTS FOR FOAM STIMULATION

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ABSTRACT

Foamed fluids have indeed become recognized as effective fluids for stimulation treatments. The unique properties of foam make it particularly suited for stimulation. The low fluid loss, low liquid content and high proppant-carrying capability of foams are among the many advantages. In addition, the lightened fluid column provides a built-in gas assist in returning the treatment fluid. Foam stimulation, however, often presents abstruse problems in fluid design and application.

Successful foam stimulation treatments require careful design of foam quality, bubble texture and half-life. These design features are influenced not only by fluid volume and gas control, but also by surfactant and stabilizer selection. A variety of liquids can be foamed, such as fresh water, brines, acid, alcohol, hydrocarbons and combinations thereof. Thus, there is growing need to understand the chemical phenomena involved in producing high quality, stable foams in all these systems.

This paper presents a review of the surfactant types commonly used as foaming agents. These surfactants may be classified by their ionic nature, which often influences performance. Anionics (soaps), non-ionics (alkyl polyoxyethylene), amphoterics and cationics (amine derivatives) are available for use as foaming agents. The performance of such additives in water, acid, alcohol, and hydrocarbon systems is compared.

In addition, the chemical stress factors which must be considered when selecting surfactants for a foam treatment are outlined. These include formation character, interaction with other fluid additives, and surfactant wetting properties. Techniques for stability enhancement are discussed.

INTRODUCTION

Foam has been shown to be an effective and economically attractive stimulation fluid especially capable of improving production in low permeability, low pressure wells. Many papers describing the mechanical design procedures for foam fracturing treatments have been circulated; however, the full potential of foam has yet to be realized.[1]

Foams used in stimulation of hydrocarbon reservoirs are composed of a discontinuous gas phase dispersed in a continuous liquid phase containing a surfactant foaming agent. The liquid phase may be fresh or salt water, acid, lease crude, condensate, or alcohol.

The gas phase typically utilized in foam stimulation is nitrogen; however, other gases can be used as well. Nitrogen is preferred because of its availability and adaptability in the field. It has several advantages over other gases in that it is completely inert and is, therefore, compatible with all fluids. In addition, nitrogen is much less soluble in treatment or produced fluids than other common gases such as CO_2. This means that with nitrogen, less gas is required to produce a foam, so storage and transportation costs are minimized. Lower solubility also means that more gas is available to assist in flowback after completion of a job.

The composition of a foam is described by the volumetric gas content, called foam quality (Q), and half-life ($t_{\frac{1}{2}}$). Foamed fluids generally contain 65-90% gaseous phase and are identified as 65-90Q foams. The time required for one-half of the original liquid phase to drain from a static foam column is referred to as the half-life. Half-life is an indicator of the foam stability.

Design factors such as injection pressure, fluid volume, bottomhole temperature, bottomhole pressure, and turnaround time are indeed important to the generation of foam. However, the success of foam treatments is also dependent on chemical factors. Foamer selection, surfactant type, chemical compatibilities, fluid systems, and formation type must all be considered in the design of the foam treatment. The following text addresses such variables. Surfactant types and their utility in specific fluid systems are discussed with particular attention paid to chemical incompatibilities and limitations.

ADVANTAGES OF FOAM

Foams provide excellent fluid loss control, proppant-carrying capacity, and other various advantages associated with low liquid content.

Fluid Loss Control

Control of loss of fluid to the formation is predominantly the result of the physical texture of the foam. As the foam bubbles gather at the formation face, they form multiple film faces across the entrances to the pores. The differential pressure required to deform the bubbles and force them into the pore spaces increases with penetration distance. This high differential pressure helps prevent further leak-off. The inherent fluid loss control eliminates the need for solid fines or chemical fluid loss agents and leaves the reservoir environment clean so that maximum conductivity may be achieved. Furthermore, since most foam treatments do not require gellants, no break times are necessary; and the well can be flowed back immediately.

Proppant-Carrying Capacity

Bubble texture is also instrumental in the ability of foam to transport proppant. Due to the close interaction of the foam bubbles, proppant particles 5 to 10 times the size of an individual bubble can be supported. As a proppant particle falls through static foam it must push aside and deform the bubbles in its path. The weight of a grain of sand is not enough to alter the integrity of the high surface energy bubbles. Thus, the sand fall rate is low.

Since the sand settling rate in foam is slower than in conventional viscous or crosslinked fluids, the sand is carried farther into the formation.[1] Individual proppant grains which are totally surrounded by bubbles are uniformly distributed throughout the fracture even at very low pump rates.

In acid treatments, foam bubbles suspend solids and fines generated by the reaction of the acid with formation rock. This minimizes the conductivity reduction often associated with lodging of fines in pores.

Low Liquid Content

Other advantages of foam are related to low liquid content. Since the liquid portion of foam constitutes only 20-30% of the total treatment volume, foams are beneficial in the treatment of clay-bearing formations and formations which tend to absorb liquids. When treating with foamed KCl or methanol/water mixtures, the minimization of fluid contact with water-sensitive surfaces reduces clay swelling, migration of fines, and fluid imbibition. In acid treatments, less active acid comes in contact with the rock matrix and formation face. The reduction of the reaction rate allows deeper acid penetration, which often results in longer fractures with higher conductivity. The low fluid content also makes foams particularly suitable for treatment of low pressure reservoirs in that it results in a lower hydrostatic head.

The gas phase within a foam is compressible, thus pressure and temperature changes cause its volume to change. As the well is flowed back, expansion of the gas causes high velocities which aid in the recovery of fluids.

VISCOSITY

The rheology of foam, which has been the topic of many papers, is influenced by a variety of factors including foam quality, bubble texture, shear stress, pressure, and temperature.

Foam quality, as previously defined, refers to the volumetric gas content of a foam. It is crucial to the many favorable characteristics associated with foamed fluids. Fluid loss control, viscosity, liquid content, and proppant-carrying capacity are all dependent on foam quality.

Since the internal gas phase is compressible, foam quality varies with temperature and pressure. During a foam treatment the average bottomhole temperature is considered to stabilize while pumping. On the other hand, bottomhole treating pressure continually changes. In order to compensate for these changes, the gas and/or liquid rates must be monitored throughout the job.[2]

As the gas volume changes, so does viscosity. A 60 to 90 quality foam usually gives the desired foam properties. In this range, the rheological behavior of foam is pseudo-plastic at shear rates of less than 10,000 sec^{-1}. Above 10,000 sec^{-1}, the behavior is Newtonian, and the viscosity (for a given quality foam) asymptotically approaches a limiting value as shear rate increases. It has been shown experimentally[3] that the viscosity of the foam is a linear function of the foam quality and the viscosity of the liquid portion.

$$\mu_{\text{foam}} = \mu_{\text{liquid}} (1 + a\Gamma)$$

where μ_{foam} is the viscosity of the foam
μ_{liquid} is the viscosity of the liquid
Γ is the foam quality
a is an empirically-determined constant.

Therefore, viscosity of foam systems should be discussed in terms of constant foam quality.

The viscosity and quality of a foam are functions of the film thickness surrounding each gas pocket. Film thickness can be related to foam quality by[4,5]

$$d = 1/3r\ (1/\Gamma - 1)$$

where d is the film thickness
r is the radius of the bubble
Γ is the foam quality.

In foams of high quality the film thickness is relatively constant with bubble size. The most stable foams have a narrow size distribution which is strongly skewed toward small-size bubbles.[2,3,7] Fine texture foams offer maximum viscosity and resistance to shear thinning.[3,6] The pressure across the liquid skin surrounding the gas pocket of a bubble is inversely proportional to the radius of curvature. Smaller bubbles have higher surface energy and consequently are more difficult to break. This increases foam stability, fluid loss properties, and sand-carrying capacity.

SURFACTANT SELECTION

Foam quality and stability are greatly affected by the liquid phase properties. As mentioned previously, a variety of liquids - both aqueous and non-aqueous - can be foamed. As the chemical type of the fluids differ, the chemical types of surfactants which will cause foams will also be different. The surfactant chosen must combine with the liquid phase to create foam when mixed with the gaseous phase.

Solubility

Foam surfactants can be classified physically by solubility and ionic nature. Each of these characteristics are important to their performance as foaming agents. A surface-active molecule, or surfactant, is composed of two parts: an oil-soluble hydrocarbon chain and a water-soluble group. The molecule will normally have a stronger affinity for either oil or water, which classifies it as oil-soluble or water-soluble.

The carbon chain length dictates solubility; and the longer the hydrocarbon chain, the lower the solubility in aqueous media. Chain length, or solubility, also affects foam quality and stability. For instance, water-soluble sulfonates are most commonly used to foam fresh water, brines, and salt (KCl, NaCl) solutions. Sulfonates, like other surfactants, are composed of an oil-soluble carbon chain and a water-soluble group, which is $-SO_3$ in this case. In the formation of a bubble the water-soluble, or hydrophilic, $-SO_3$ groups align with the aqueous phase while the oil-soluble portions are repelled. This phenomenon allows an oily film to form around the internal aqueous layer and gas pocket in the formation of foam.

Often, a single carbon link will influence the development of a stable oily film. For example, 3-carbon chains are more soluble than 4-carbon chains in water, but are less effective water foamers. This suggests that surfactants which are too soluble in the selected media often do not propagate the formation of the oily layer necessary for foam stability.

Although solubility does appear to regulate bubble structure somewhat, ionic character probably has more influence over the quality of the foam. Surfactants may be ionically positive (cationic), negative (anionic), neutral (nonionic), or mixed (amphoteric). The application of these ionic types depends primarily on the fluid system used.

Anionic Foamers

Anionic surfactants are organic molecules whose water-soluble group is negatively charged. Typical examples of these are sulfates and sulfonates. The activity of an anionic surfactant is vested in the acidic group which performs best when neutralized. Thus, anionics generally are the most effective fresh water, salt water, and brine foamers. They tend to produce very high quality, fine-textured, stable foams at relatively low concentrations. Because of superior foam development in water, anionics are particularly useful in aqueous foam-fracturing treatments involving proppant placement. In addition, the improved stability means anionic foams can be used in many workovers including removal of sand, mud or other debris from a well; stabilization of back pressure on the casing side during stimulation; bullheading for well kickoff; and pumping down coiled tubing.

Anionic foamers, because of their availability and low relative cost, are widely used; however, the ionic nature of these molecules is sometimes restrictive. Incompatibilities between anionic foamers and cationic additives (e.g., clay stabilizers, non-emulsifiers, or friction reducers) often cause substantial reductions in foam quality and half-life. Bubble texture generally changes considerably - from frothy and fine-textured to clear, large bubbles which prove to be much less stable. Insoluble precipitates also may form when anionics and cationics are combined. In applications requiring clay control agents or similar cations, amphoteric or nonionic water foamers should be used.

Anionics also are limited to certain formations. Since they adsorb to positively-charged surfaces, anionic foamers leave some formation types oil-wet. Oil-wetting a normally water-wet formation can reduce permeability to oil by as much as 85%. Consequently, anionics lose their utility in limestone or dolomite formations which carry a positive surface charge under normal reservoir conditions.

Cationic Foamers

Cationic surfactants are organic molecules whose water-soluble group is positively-charged. Most cationics are amine compounds such as quaternary ammonium chloride. Like anionics, cationics also perform best in neutralizing media. Since cations contain a basic water-soluble group, these molecular types are most applicable in acid foam treatments. Because of their ionic nature, cationics offer several advantages. For example, they are compatible with most corrosion inhibitors, clay stabilizers, and bactericides which are also positively-charged. In fact, cationic foamers often aid in such functions.

Other benefits involve surface activity. Cationics normally adhere to anionic areas of a formation surface working to oil-wet sand, shale, or clay. The advantages to this are two-fold. By oil-wetting water-sensitive formation surfaces, clays are protected from water contact, so swelling is minimized. In addition, by oil-wetting spots on the formation face, cationics reduce the reaction rate of the acid with those areas. Acid will preferentially spend on water-wet segments, resulting in rock pillars between fracture faces which provide permanent flow channels.

The physical appearance of cationic acid foams resembles that of anionic water foams, since similar foam quality, bubble texture, and stability are attainable.

Amphoteric Foamers

Amphoteric foamers include both acidic and basic groups in the same molecule. In acidic pH, the basic portion of the molecule ionizes, making the compound surface active and predominantly cationic. In basic pH, the acidic group neutralizes, and the molecule behaves as an anionic surfactant. Most amphoterics exist in a dielectric state at neutral pH values and so perform comparably with many nonionic surfactants. Amphoteric surfactants function well in most aqueous or acid systems because of their adaptability to broad pH ranges; however, they often do not produce as high quality or as stable foams as fully-charged anionic or cationic surfactants.

Most amphoteric molecules possess both quaternary ammonium and anionic radicals, where the anion is either a carboxyl, sulfonate, or sulfate. The compatibility of the amphoteric molecule with other surfactants depends on the type of anionic and cationic radicals involved. Specific tests must be run to determine possible incompatibilities. In general, amphoterics have a broader range of compatibilities than anionic or cationic surfactants.

Nonionic Surfactants

Nonionic surfactants are molecules which do not ionize and therefore remain uncharged. The vast majority of nonionic surfactants are condensation products of ethylene oxide or propylene oxide with a hydrophobe. The hydrophobe is usually a high molecular-weight material with an active hydrogen atom.

Nonionics, like amphoterics, do not always produce the high quality, stable foams characteristic of the anionic or cationic surfactants. However, they probably provide the widest range of application. Nonionic surfactants, of different chemical types, can be used to foam both aqueous and non-aqueous fluids.

For foaming methanol or hydrocarbons, nonionic fluorosurfactants are particularly useful. In non-aqueous systems, fluorocarbons produce higher quality, more stable foams than hydrocarbon-type foamers. The bubble texture of fluorocarbon-initiated foams is much finer than conventional non-aqueous foams. In methanol/water systems containing as much as 30% methanol, anionic water foamers provide high quality, stable foams. In 30% to 70% methanol in water solutions, a nonionic hydrocarbon-type foaming agent is most effective; and in 70% to 100% methanol, nonionic fluorosurfactants are best.

Nonionics also can be used to foam water or acid. They generally are more compatible with surfactant additives of various ionic natures. However, nonionic surfactants have other peculiar limitations. Since most nonionics are derivatives of ethylene and/or propylene oxide, their solubility in water is directed by hydrogen bonding. The attraction of water for the oxygen of the ethylene oxide is reduced at elevated temperatures and/or high salt concentrations, causing most nonionic surfactants to separate from solution. Such solubility problems can limit the use of many nonionic foamers to low temperature, fresh water treatments.

Surface Tension

It is essential that surfactants used in foaming aqueous fluids reduce the surface tension of the liquid media. Since foaming requires energy to create new surfaces, the lower the surface tension at the surface between the gas and the liquid, the less the amount of work required. Surface tension reduction is also necessary to reduce formation damage due to capillary imbibition. It has been shown that the surface tension of water containing a given surfactant decreases linearly with concentration of the surfactant to a minimum surface tension. Increased concentration of the surfactant does not reduce the surface tension further. Typically, the concentration of surfactant required for foaming is greater than this critical concentration for maximum reduction of surface tension. Table 1 presents surface tension data on several surfactants in various media.

The wetting behavior of surfactants used in foaming must be considered when selecting the appropriate foaming agent. Wettability is simply a term used to indicate whether a surface will be preferentially coated with a film of oil or water. Most formation surfaces have varying degrees of wettability. That is, since the formation surface in most cases is somewhat heterogeneous, the water-soluble portion of a surfactant will be attracted to some areas and repelled from others. The result is one of mixed wettability.

Wettability tests performed with different types of foamers showed the expected correlation of wetting behavior on sand with ionic character of the surfactant. None of the surfactants tested showed strong water or oil-wetting; however, preferential behavior was distinguishable, as shown in Table 2. The cationic and amphoteric foamer molecules adhere to the negatively-charged sand surface due to electrostatic attraction. The non-polar portions of the molecule are exposed, thereby creating a film of oil on the formation surface. In some cases, large organic cations in the surfactant molecule replace the water-absorbing cations (usually Li^+ or Na^+) on a clay surface. The surfactant cations attract water less strongly than Li^+ or Na^+, and the clay becomes non-swelling.

Anionics are repelled by the negative surface charge of sand leaving the inorganic, water-soluble portion of the molecule exposed to render the surface water-wet.

FOAM STABILIZING AND BOOSTING TECHNIQUES

Various foam-stabilizing additives may be used in conjunction with foaming surfactants to increase half-life. Viscosifiers often increase the half-life of foam by as much as three times. In water, 2% KCl, or up to 30% methanol, guar gums or cellulosic polymers may be used to enhance foam stability. Modified guar gums may be used to stabilize low-concentration acid systems as well; however, viscosity typically does not last long. Xanthan gums, which maintain viscosity over a longer period of time in high acid concentrations, are preferrable foam stabilizers. Liquid gellants are also available.

Methanol (50-100% in water) and hydrocarbon systems typically require stabilization. Carboxymethyl cellulose provides adequate stabilization of methanol systems up to and including 100% anhydrous methanol. Phosphate esters, fatty acids, and aluminum octoate are common stabilizers for hydrocarbon systems.

The concentration of gellant used to stabilize foam is important to foam quality. When base fluid viscosity is increased, foam volume will proportionally decrease. Viscosity of 15-20 cp provides sufficient thickness for foam stabilization.

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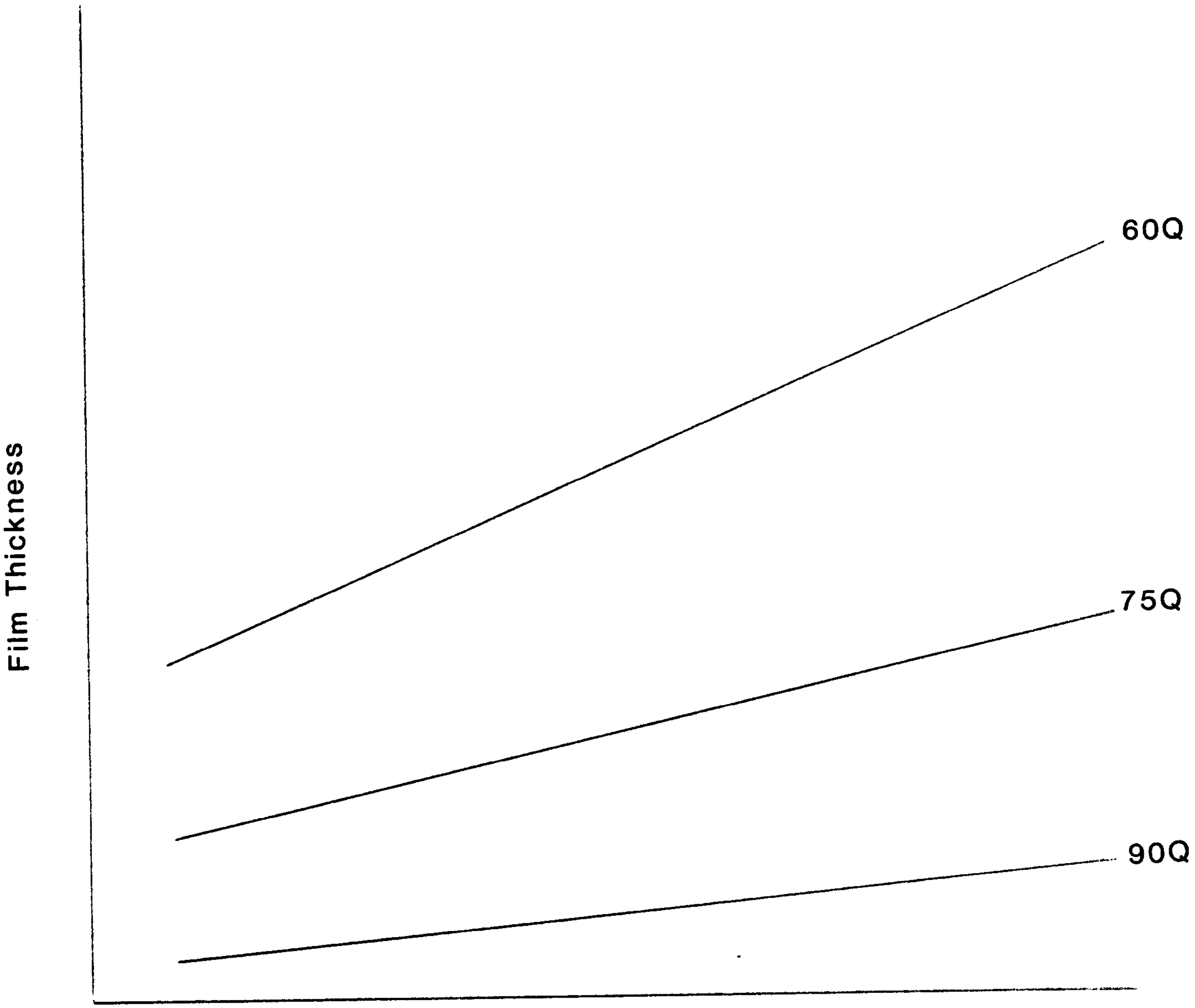

FIGURE 1 — AVERAGE BUBBLE RADIUS

Foam Volume vs Loading 2% KCl

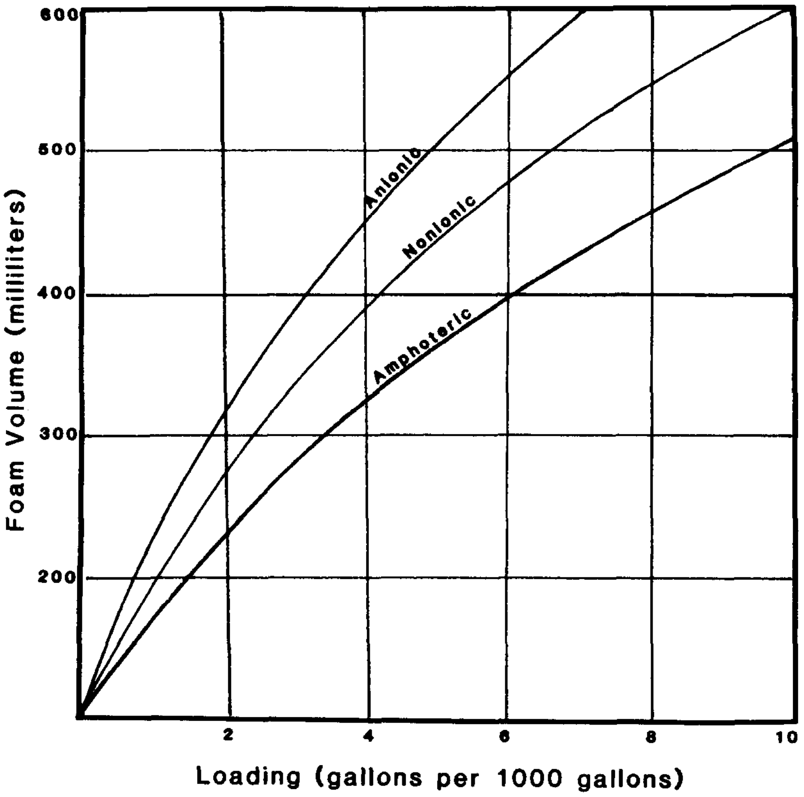

FIGURE 2

Foam Volume vs Loading
2% KCl with Clay Stabilizer

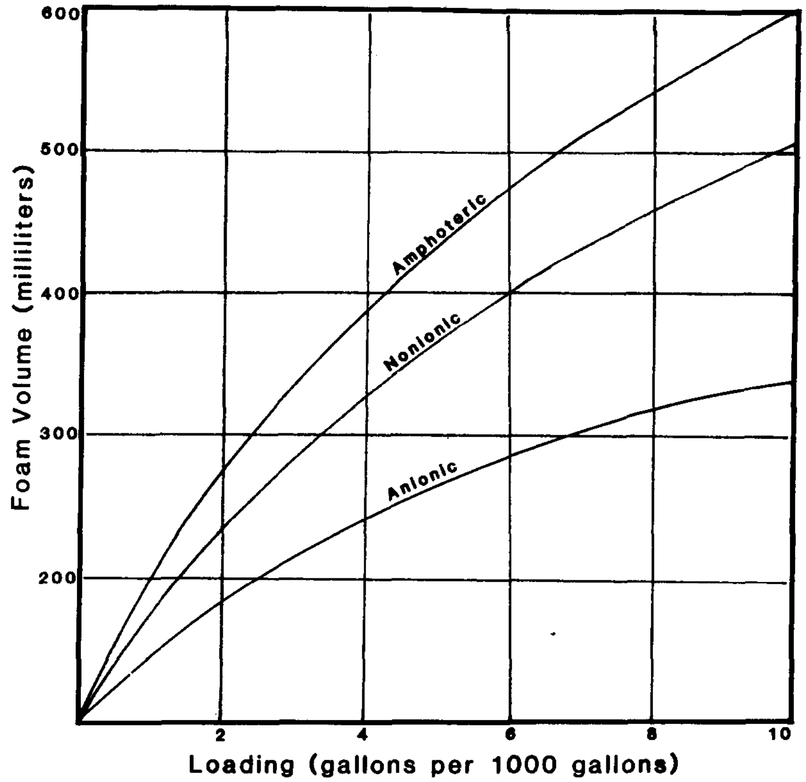

FIGURE 3

TABLE 1

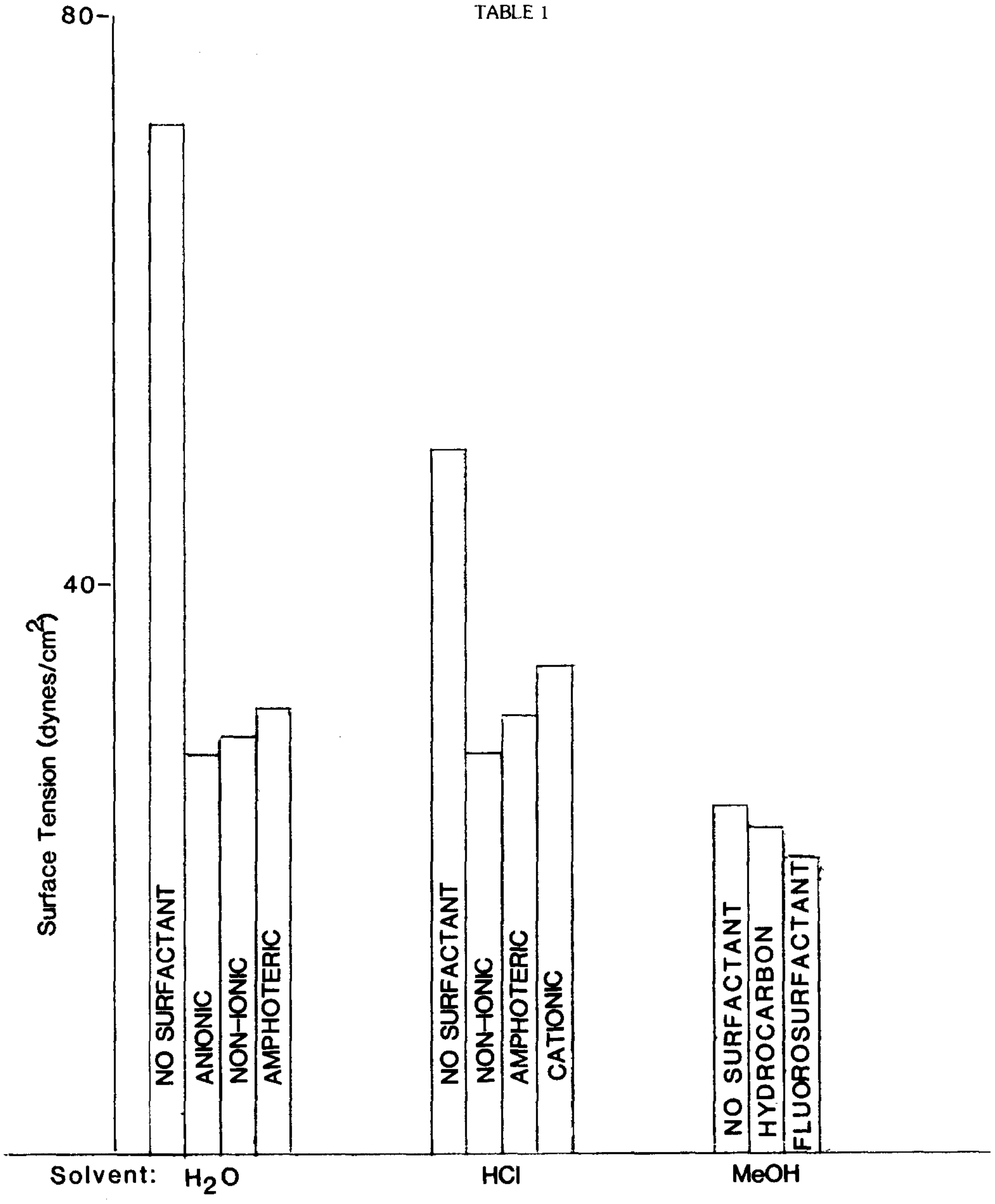

TABLE 2 — WETTING CHARACTERISTICS

	WETTING OF SAND
ANIONIC FOAMER 1	WW
CATIONIC FOAMER	OW
AMPHOTERIC FOAMER 1	OW
NONIONIC FOAMER	WW
ANIONIC FOAMER 2	WW
AMPHOTERIC FOAMER 2	OW

pH neutral solution