DEVELOPMENT OF FOAMS

For Use In

FOREST FIRE CONTROL

a preliminary report

by

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INTRODUCTION

In forestry, one of the principal problems encountered is that of the control of forest fires. Research has been carried on for many years in efforts to increase the effectiveness of present methods and also to discover new and better techniques. There are still large annual forest fire devastations of valuable North American timber — a natural resource requiring many years for replacement.

In forests in central Europe, where the terrain is not mountainous, it is a common practice to build permanent protective fire lanes at frequent intervals.[1] It is thus possible, in the event of a forest fire, to bring motorized fire fighting equipment in rapidly. Suppression of the fire can be accomplished with water, if the fire is small.

In Canada and in the United States, areas with adequate fire-breaks are few and accessibility is more of a problem. In the Rocky Mountain and Coastal regions in both countries, where the terrain is un-negotiable for mobile fire fighting equipment, forest fire control work is done by either:

(a) massive air drops of water, or of water with additives,

(b) setting backfires, a risky practice in some instances,

(c) individual fire-fighters afoot — carrying individual backpack pumps containing several gallons of water, hand equipment for beating out small ground fires, shovels, etc.

Recently-developed light-weight portable motorized pumps are, of course, very useful where water is available, particularly in regions not accessible to motor driven vehicles.

The idea of adding fire retarding chemical compounds to water to increase its extinguishing effectiveness per gallon, was suggested as early as 1931.[2] The ammonium phosphates (monoammonium) (diammonium) have

1. Mr. Liebeneiner, West German Forestry Officer, during his visit to the Petawawa Forest Experiment Station during August 1966, gave these figures for German forest practice: fire land roads about 30 feet wide, and about 900 feet apart.

2. Evaluation of Forest Fire Retardants, U.S. Forest Service Research Paper 64 (1962), by Hardy, Davis, Rothermal.

been consistently studied for this purpose, but until recently they have not been used against forest and brush fires to any extent.[3] Forest cover properly treated with either monoammonium phosphate or diammonium phosphate solutions in water will not support combustion.

In many cases, either water or water solutions tend to bounce or run off the foliage during or after application. This is particularly true in drops of liquids from low-flying aircraft. In some regions chemical agents are added to water to increase its viscosity tremendously. Such water dispersions are called "thickened water". These have a special ability to cling to foliage. Agents serving the above purpose include: Gelgard[4], Hercules CMC (carboxymethyl cellulose)[5], ammonium pectate[6], alginate gels[7], Fire-Trol[8], Firebrake and Borate XPL-113[9], etc. Some work has been done with "wet" water, water to which chemicals have been added to reduce surface tension and thus to increase its ability to wet surfaces and to spread out over them.

Another method used, for keeping applied water in proper locations, employs water solutions blown up into foams. Foams inflated with carbon dioxide have been used for a long time to suppress oil fires. Carbon dioxide is about $1\frac{1}{2}$ times as heavy as air, and of course does not support combustion. The carbon dioxide foam floats on the oily surface, until the heat from the oil fire causes the bubbles to burst. The heavy blanket of released carbon dioxide continues to keep out oxygen needed for combustion. Such a "blanket" is very useful in extinguishing fires on flat, horizontal surfaces, especially when the surfaces are bounded by vertical walls which help to keep the heavy carbon dioxide foam or gas in place.

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3. Monsanto Technical Data Sheet TDS I-226, December 1963, page 3, Monsanto Chemical Company, St. Louis, Mo. 63166.

4. A synthetic dry polymer product of the Dow Chemical Company, Midland, Michigan 48640.

5. Hercules Technical Data Bulletin No. 405 B, No. VC - 442, Hercules Powder Company, Wilmington, Delaware. Careful addition of selected salts of trivalent metals, (especially aluminium) to carboxy-methyl cellulose, leads to the formation of gels of controlled stiffness.

6. Fire-retarding diammonium phosphate may be added to the ammonium pectate dispersions. Pectate[4] is available from the Ventura Coastal Corporation, P.O. Box 69, Ventura, Cal. 93002.

7. Alginates have been studied in the above application. Keltex FF was available from the Kelco Company (Canadian representatives: Charles Tennant and Co. Canada, Ltd.) 34 Clayson Rd., Weston, Ontario, Canada.

8. Ammonium sulfate fire retardant, plus attapulgite clay, available from Arizona Agrichemical Corporation, Pheonix, Arizona.

9. Sodium calcium borate, etc., produced by U.S. Borax and Chemical Corporation, Los Angeles 5, California.

Combustible forest cover areas are seldom of such a nature, except possibly where short grasses occur on level land. Carbon dioxide-inflated foams could be somewhat useful in laying down fire-barrier lanes on such cover. However, upon the approach of the advancing fire, the foam might disintegrate rapidly, and the released carbon dioxide blanket could be blown away almost instantly, leaving no barrier protection.

A further important factor, in considering carbon dioxide foams, is the necessity for transporting relatively large quantities of bicarbonates and acidic reagents, to liberate carbon dioxide. Chemical calculations show that, for generating enough carbon dioxide to inflate a carbon dioxide foam of sufficient volume to lay down a fire barrier 100 feet long, only two feet wide and only three inches deep, more than 16 pounds of sodium bicarbonate and, say, phosphoric acid, are required. It is not logical to transport such large quantities of chemical reagents, and the necessary equipment (pressure tanks, meters, mixing equipment, etc.).

With these considerations in mind, this study has been confined to air-inflated foams. At the outset, two pertinent questions were considered:

(a) Since any foam will be likely to partially disintegrate before the advancing fire reaches it, is there any advantage in using the liquid (water, etc.) in the form of a foam, rather than in liquid form, and

(b) can formulae be developed, in which there are sufficient concentrations of fire retardant chemicals in the liquid left after the foam bubbles burst, to stop the spread of fire into the protected region - something which the small amount of water (from the foam) alone can scarcely do?

It is our belief that the answer to the first question is yes, for two reasons:

(a) The foam, when applied to vegetation, has much less tendency than water to bounce or run off, and

(b) probably a more even coverage is sustained. Water alone flows more easily to the lowest point of the leaf to which it clings, and then drops off.

The approach to the second question seems obvious. Try to work fire-retarding chemical compounds into the foam-forming liquid without destroying the foam-forming properties of the liquid.

OBJECTIVES

Research began with the following three goals:

(a) To find, or if necessary, to develop, laboratory test methods for evaluating quantitatively, the important properties desired in the foams.

(b) To apply these evaluation procedures to several good foams now available, and to new air-foams developed in the course of the project - in order to find which ones possess the largest number of desired properties to an appreciable degree.

(c) To experiment with additions of fire-retarding monoammonium phosphate and diammonium phosphate, in order to find which of the best foam-forming solutions would tolerate 2% additions of these compounds, without appreciable loss in foam forming capabilities. Such concentrations have been shown[10] to yield around 80% of the fire-retardant effectiveness of much higher concentrations.

The third objective was expected to pose some problems, since in many cases, stable foam formation depends upon concentration of the foam-stabilizing agent molecules (for example, protein molecules) in the interface between air and the liquid in the foam bubble walls. The presence of "impurities" (in this case, of one of the phosphates) could disturb these conditions, and damage the foam-forming capabilities of the foam stabilizer.[11]

SOME FOAM THEORY

Foam stability can be due to the presence of proteins (for example gelatin) which concentrate at the solution-air interface to form a kind of solid "skin". It may be obtained by using substances such as saponins which give the surface layer of solution a greater viscosity than the bulk of the solution. Substances (for example alcohols) which produce the Marangoni effect[12] (in these cases, the surface viscosity is low), or upon the presence of the so-called colloidal electrolytes - which when dispersed in water, yield long-chain ions with either positive or negative electrical charges, will also produce foam stability. The latter colloidal electrolyte agents are classified respectively as either cationic or anionic.

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10. Fire-extinguishing Effectiveness of Chemicals in Water Solution, Howard D. Tyner, Ind. Eng. Chem. 33 60-65 (1941).

11. J.J. Bikerman, Foams and Emulsions, Ind. Eng. Chem. 57 (No. 1) 56-62 (1965).

12. See reference 11. When such a foam film is ruptured by, for example, a droplet of mercury falling through it, the underlying liquid (with a greater surface tension) is exposed, and the high surface tension existing, tends to close the puncture.

Respective examples are: stearyldimethylbenzylammonium chloride (Triton X-400), and sodium alkylaryl polyether sulfonate (Triton X-200).[13]

The colloidal electrolytes, particularly those yielding negatively charged long-chain anions, constitute a very widely used class of foam stabilizers. A cross section of the bubble wall of a foam generated with such an agent[11], consists of two layers of such long ions, standing on end at the liquid-air interfaces, with their hydrocarbon ends pointed toward the air. Between the two layers is the liquid phase, which completes the sandwich. Within the liquid phase, there are two additional corresponding layers of oppositely charged counter-ions.

For air-water foams stabilized by the presence of gelatin (a protein) the stability of the foam can be quite dependent upon the p^H of the foam-forming dispersion.[14] For dispersed proteins, in general, the signs of the electrical charges on the dispersed colloidal particles are dependent upon the hydrogen in concentration, and can be changed by a proper modification of the p^H. Even for solutions of soaps, there exists an optimum p^H for maximum foam stability.[15]

In general, the foaming ability, of a water preparation is related to the amount the surface tension of the water is lowered by the presence of a foam stabilizer, but the stability (life) of the foam appears to have little relation to the surface activity present.[16] Mixtures of surface active agents may provide a many-fold increase in foam-forming ability in some cases.

Obviously the term "good foam" is a relative term, and the "goodness" of a foam can be evaluated in terms of the extent to which certain desired foam properties are present. For example, if a long lasting foam is desired, then one criterion of "goodness" is the length of time the bubbles persist before collapse. Since small bubbles tend to grow into larger ones a small-bubble foam tends to have a longer life.

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13. Products of Rohm and Haas Company. See Rohm and Hass Surfactants Handbook or Physical Properties (1965) page 2, Rohm and Haas Co., Independence Mall West, Phila. Pa. 19105.

14. This foam is the most stable at the isoelectric point (at about p^H 4.8) at which also the solubility of gelatin is at a minimum. References: Colloidal and Amorphus Materials, Lewis, Squires, Broughton (1943) MacMillan Company; Advanced Organic Chemistry, Fieser and Fieser (1961) Reinhold Publishing Corporation.

15. Miles and Ross, J. Phys. Chem. 48, 280 (1944).

16. A Short Textbook of Colloid Chemistry, 2nd Ed., Rev., Jergensons and Straumanis (1962), MacMillan Co.

DEVELOPMENT OF FOAM EVALUATION METHODS

Methods have been suggested and used[17] for measuring several of the important properties of foams. Properties frequently measured include: foaminess (the ability to form foam), and foam stability (lifetime, persistence, the reciprocal of the rate of foam collapse, etc.).

A number of recognized and suggested methods of measuring foam characteristics were tried and modified to permit an evaluation of various foams. Several other techniques were developed with the objective of providing a measure of the effectiveness of different foam stabilizers. Some of these were particularly revealing, in our search for agents which would:

(a) produce a satisfactory foam;

(b) produce this in the presence of concentrations of approximately 2 per cent of mono- or di-ammonium phosphate.

This criterion for a satisfactory foam was the ability to last at least half an hour, preferably several hours. A moderate rate of foam expansion was sought with foam volume to foam producing liquid ratios[18] of somewhere between 10 and 50.

Foam volume ratio sizes depend much upon the type of equipment used to generate the foam. In general, if compressed air is admitted through a capillary tube whose exit is under the liquid surface, the foam bubble size is influenced by the rate of separation of the bubbles from the nozzle (a high rate gives smaller bubbles),by the liquid surface tension size (lower surface tension gives smaller bubbles), and obviously also by the radius of the capillary.[16]

Before the evaluation methods were finally adopted for the routine testing of foam-forming agents, preliminary exploratory studies were necessary. These were carried out with two commercially available foam-forming agent concentrates diluted with water.

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17. For example, the Ross and Miles pour foam test to measure the foaming ability of a liquid. Reference: Ross and Miles Oil and Soap 18, 99 (1941). See also the ASTM Standard Method of Test for Foaming Properties of Surface-Active Agents, ASTM Designation D 1173-53 (1965). See also reference 15 this report.

18. We found such ratios for two different commercially available foam producing liquids, using the dense foam generator described below.

PRELIMINARY RESULTS OBTAINED

The exploratory evaluation tests were carried out with:

(a) a feather-extract product produced and marketed in several modifications, by Laurentian Concentrates, Ottawa, Canada.

(b) JET-X Foam Liquid, a product of Bliss-Rockwood Company, Worcester, Massachusetts.

The exploratory tests yielded some interesting results, which proved to be quite helpful in setting up final routine foam evaluation procedures.

Our preliminary studies were all with small bubble size (low-expansion) foams. The JET-X ('high expansion') Foam Liquid solutions could, under suitable conditions, be used also to generate small bubble foams.

A. Feather-Extract Foams

Measurements were made of the maximum volume of foam produced by the conversion of 100 ml of foam-producing water dispersion, as a function of the per cent concentration (in grams of agent per 100 ml of dispersion) of foam forming concentrate. Data obtained are summarized in the table on the following page, together with surface tension values for the corresponding solutions or dispersions. As is evident from the data and graphs following, (Figures 1 and 2), the foam forming abilities and the surface tension lowering were both found to be linear functions of the common logarithms of the concentrations of agents. Some relation between foam forming ability and lower surface tension is generally accepted.

Table 1.

Properties of Feather Extract Foam Concentrate Dilutions

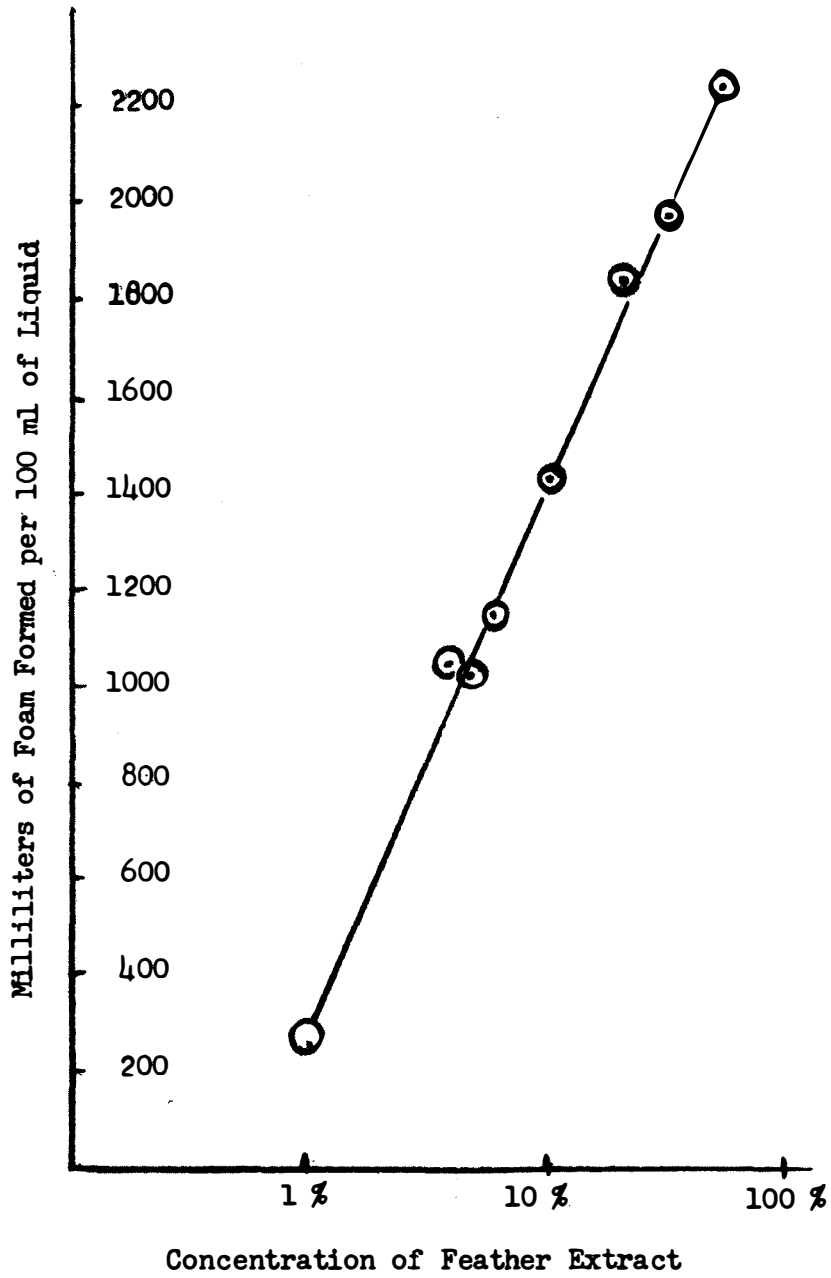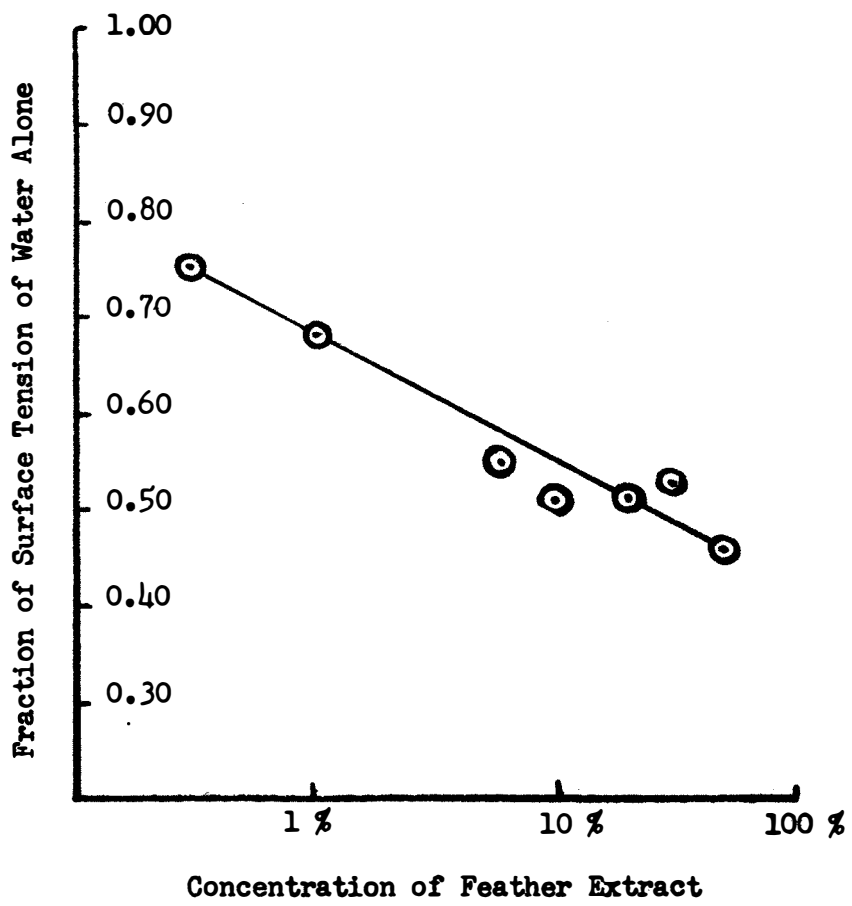| Concentration %	Surface Tension fraction of that of water alone	Foam volume, ml per 100 ml liquid
0.3	0.75	---
1.0	0.68	275
4.0	--	1050
5.0	--	1025
6.0	0.55	1150
10.0	0.52	1425
20.0	0.51	1850
30.0	0.53	1975
50.0	0.46	2250

Figure 1

Figure 2

The foam generator used in these measurements was of a design suggested by Dr. W.L. Ball.[19] An ordinary 500 ml Pyrex filter flask was used in reverse direction. Compressed air (5 pounds per square inch) was admitted through a glass inlet tube (a 7 mm tube constricted on the exit end, to about 3mm) extending through a 1-hole rubber stopper, to the bottom of the flask. A foam exit rubber tube was attached to the flask side arm. A final short section of glass tubing led the foam into a 2000 ml glass graduate cylinder, used as the foam receiver. While relatively large bubbles were blown in the flask itself, they were very small at the exit location. The small-bubble low-expansion foams were quite stable, and the foam volume measurement was easy. In the case of the lower concentration dispersions, however, the foam drainage was rather rapid. The separated liquid was returned quickly to the generator and run through it again, to convert it back into foam.

It will be noted that the maximum foam volume (to liquid volume) ratio realized for a 30% concentration of the pure concentrate, as we received it, was about 20. The volume ratio found for around a 5% concentration was about 10. Foam volume ratio measurements for concentrations under about 5% were difficult, since the foam was quite "soupy" and reverted rather rapidly to the liquid state. An item of further interest is that the surface tension of even a 20% dispersion was reduced to only about one half of the value for water alone.

B. JET - X Foams

Measurements similar to the above were made with varied concentrations of JET-X Foam Liquid dilutions. Results obtained are summarized in Table 2 below and are shown in graphs: Figures 3 and 4:

Table 2.

Properties of JET - X Foam Liquid Dilutions

Concentration %	Surface Tension fraction of that of water alone	Foam volume, ml per 100 ml liquid
0.1	0.81	—
0.2	0.68	(approx) 175
0.4	0.54	—
0.6	0.43	525
1.0	0.41	800
2.0	—	975
4.0	0.37	2325
7.0	—	3500
10.0	0.36	—
15.0	—	4925
20.0	—	5500
100.00	0.33	—

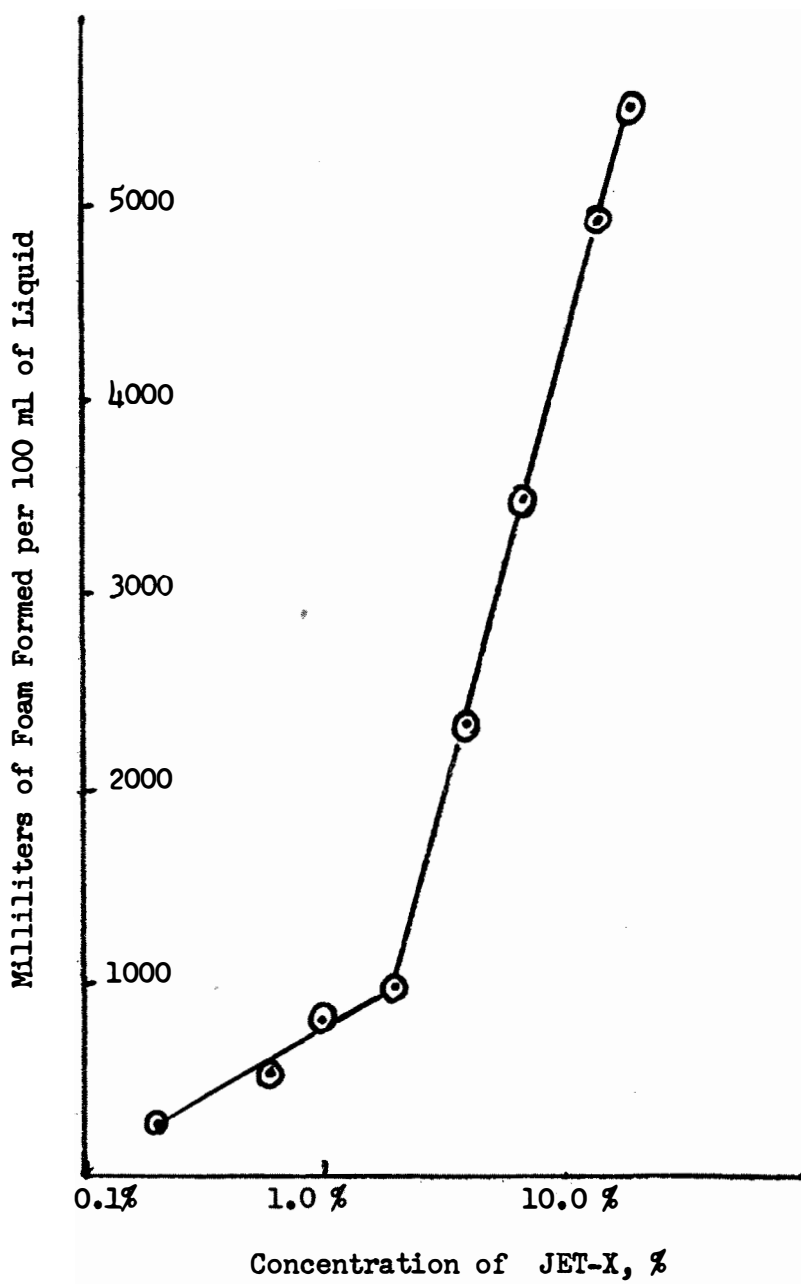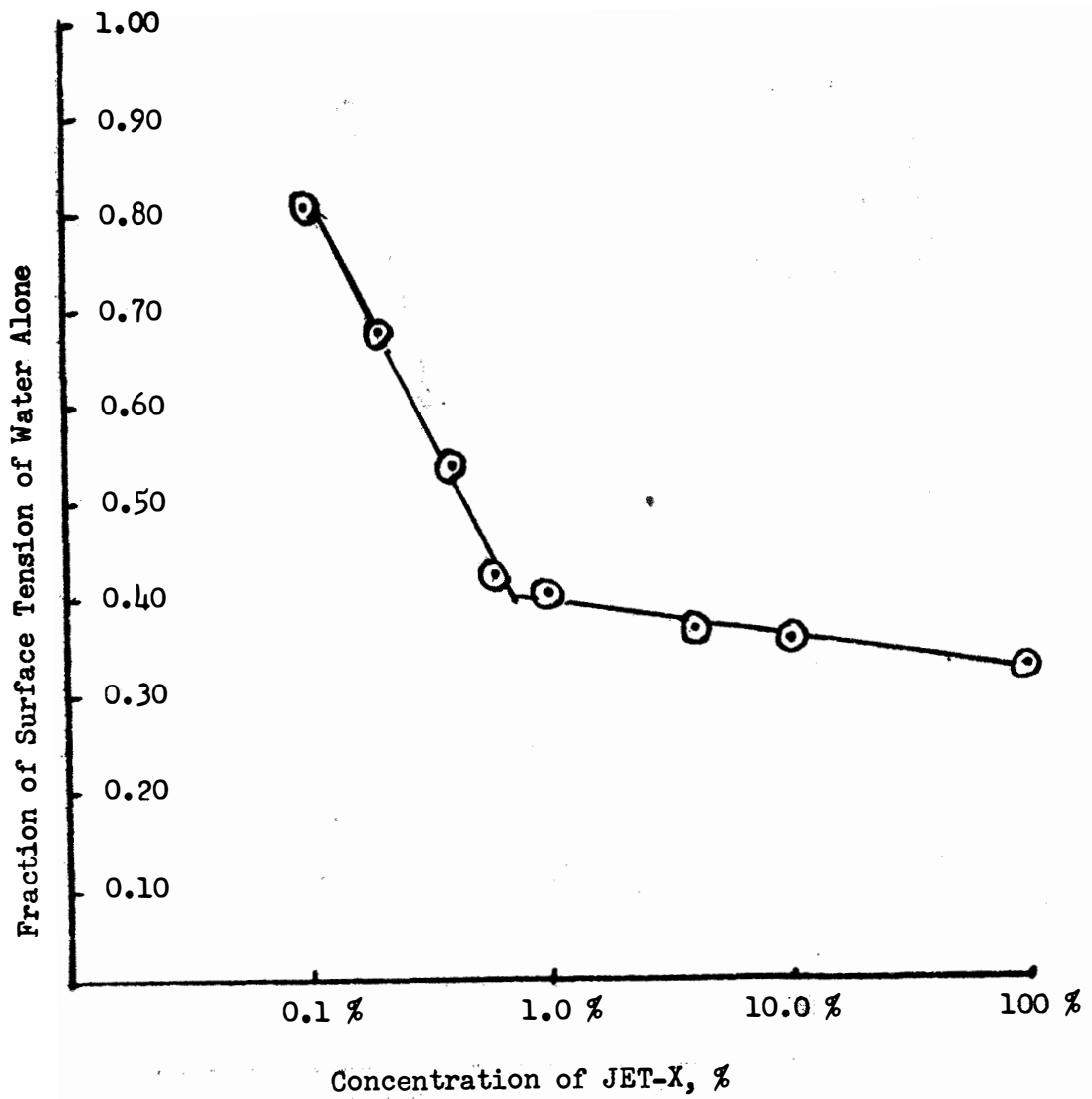19. Dr. W.L. Ball, Department of National Health and Welfare, Ottawa, Ontario.

Figure 3

Figure 4

The foam volumes and the surface tensions of the foam-forming dilutions of JET-X also were found to be linear functions of the logarithms of the concentrations of foam stabilizing agents. However, for this agent, breaks were found in both curves (Figures 3 and 4) in the vicinity of 1% concentrations. The significance of these changes in relationships is not immediately evident. The concentration of pure foam-stabilizing agent in each of the dilutions was not known.[20] A study of the significance of these breaks and the concentrations at which they occur for different agents will be undertaken presently. Such information may add to the understanding of relations between surface tensions of foam-forming solutions or dispersions, and the foaming abilities of these. It is of interest that, despite the breaks in both curves, the foam-forming ability seems to be related closely to the lowering of the surface tension of water, over the wide ranges in concentration studies.

One further observation: surface tension lowering to about 40% of that of water alone occurred at around 1% concentrations of JET-X concentrate, but for even 50% concentration of Feather Extract concentrate, the surface tension was reduced to no lower than 45% of that of water alone.

The foam volume ratio reached 55 for 20% concentrations of JET-X concentrate, or about three times the value found for the same concentration of Feather Extract concentrate.

The difference in foam volume ratios does not necessarily indicate a superiority of one foam-forming agent over the other. The Feather Extract agent is recommended for the formation of low-expansion foams, while JET-X is presumably an agent designed to produce much higher-expansion foams. As mentioned, a desirable forest fire retardant foam should have moderate expansion and be stable.

Combined JET-X (3%) and
Feather Extract (3%)

A combination of two foam-forming agents can give a liquid a much greater foam-forming ability than a similar total concentration of either agent used alone. Experimental runs to test the possible applicability of this principle were made with combinations of these two foam-forming agents. Results were rather disappointing, as the foam volume ratios obtained were about the same as those for 6% concentrations of JET-X alone. Further tests along this line were not made.

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20. We had no data on concentrations of active agent present, but, judging from the low density value we obtained, it must be quite high. Dilutions were all made assuming the concentrations to be 100%, so the concentrations were consistent with each other.

A trial run with JET-X (0.5%),
and 5% of an alginate (viscosity
builder for water)

In this run, the foam volume ratio was less than one-half of that realized for a similar concentration of JET-X alone. A remarkable feature of the foam was the foam bubbles were almost as resilient as rubber, and were very tough. As was mentioned in the section SOME FOAM THEORY, foam stability can be achieved through several mechanisms. The two above agents presumably could operate in quite different ways to serve the purpose. This approach should be investigated further, later on.

METHODS CHOSEN FOR EVALUATIONS

Routine evaluations were made of the following properties of foam-forming liquids, or of foams formed from the liquids, using 1% concentrations (2 grams of concentrate diluted with distilled water, to a total volume of 200 ml).

A. Compatibility (clear, or not) with 2% concentrations of diammonium phosphate, and of monoammonium phosphate.

B. Approximate p^H values.

C. Bubble wall strengths, as indicated by the maximum size of bubble which could be blown before bursting. The compressed air flow for inflation was kept at 1 litre per minute.

D. Foam stabilities were determined by a dynamic equilibrium method. Compressed air was passed into the bottom of 200 ml of foam-forming solution in a tall 2000 ml Pyrex glass graduated cylinder at a rate controlled manually by a needle valve.

The air admission rate was adjusted carefully until the foam surface at the top of the cylinder maintained an approximately constant level. In this case, the rate of foam formation, as determined by the rate of compressed air admission, was just equal to the rate of foam collapse. The method appears to be a very sensitive one. The rate of foam inflation can be determined readily by switching the air flow quickly into a water reservoir bottle equipped with a glass outlet tube. Air flow was allowed to continue until 500 ml of water was collected in a graduated glass receiver. Before collection, the 250 ml mark on the receiver was adjusted to the same level as that of the water in the reservoir bottle. The time required for 500 ml of water to be displaced from the reservoir, by the incoming air volume was determined in each case with a stopwatch. Rates of foam bubble inflation were readily calculated in terms of milliliters per second. Obviously, this rate represents also the rate of foam collapse. Low rates thus mean more stable foams.

E. **Foam life index**. At the instant the foam forming air stream was shut off, in the foam stability test, a stopwatch was started. At the time, the foam collecting cylinder was completely full (2500 ml of foam and liquid). The original volume of 200 ml of liquid was not appreciably reduced by the conversion of some of it into enough foam to fill the cylinder. Thus the original foam volume at zero time was 2300 ml approximately. After a 5 minute time period, the foam volume was read again. The volume of foam remaining, divided by 2300 ml, gives the quantity named the (five minute) **foam life index**.

F. **Foaminess**. Ten ml of foam-forming solution (1% concentration) was poured into a 100 ml glass graduated cylinder. The cylinder was stoppered, and then shaken violently, endwise, for 20 strokes. After standing for one minute, the volume of foam above the liquid was read and recorded. The volumes are those listed in Table 3, page 16.

EXPERIMENTAL EVALUATION RESULTS OBTAINED IN PRINCIPAL TESTS

The above tests were applied to water dispersions of 11 selected foam-forming concentrates or solid agents. Throughout, 1% concentrations (1 gram of concentrate or of solid agent with enough water added to make a volume of 100 ml) were used. Comprehensive data are summarized in Table 3. Figures given represent arithmetical averages of results of from 2 to 20 experimental values, with the most usual average being based upon about 5 determinations. It will be noted in Table 3 that the five types of determinations were made with a 1% concentration of foam-stabilizing agent, with a 1% concentration of foam-stabilizing agent plus a 2% concentration of diammonium phosphate fire retardant, or with a 1% concentration of foam-stabilizing agent plus a 2% concentration of monoammonium phosphate.

Of the 11 foam-forming agents thus evaluated, 2 were the above-mentioned agents which are commercially available. These appeared to have quite desirable properties, and they were included to serve as bases for comparisons in various respects with other foam-forming agents tested. They are the third and the eleventh agents listed in Table 3.

The pH values determined were for future reference purposes and served very little purpose otherwise, at the moment.

It will be noted that the maximum bubble diameters found were in several cases 2 or 3 times the diameters found for water dispersions of the comparison agents. In the cases of the two standards and of six of the other foam stabilizers tested, the bubble diameters were not much affected by the presence of the phosphates, which we believe indicates little damage to film strengths.

Table 3

EVALUATIONS OF FOAM-STABILIZING AGENTS

AGENT	Agent Number	Compatibility with 2% DAP	2% MAP	Approximate pH Values 1% Soln.	Soln.+ 2% DAP	Solution 2% MAP
Proctor & Gamble Foaming Agent	1	Clear	Clear	6 - 8	6 - 8	6 - 8
Witco Ultrapole CDA	2	Cloudy	Cloudy		-	-
Bliss-Rockwood Jet - X	3	Clear	Clear	4 - 6	6 - 8	4 - 6
Proctor & Gamble ORVUS K Liquid (anionic)	4	Clear	Clear	4 - 6	6 - 8	6
Swift & Co. Solav HE 575	5	Clear	Clear	-	-	-
Proctor & Gamble Amide #72	6	Cloudy	Milky	-	-	-
Proctor & Gamble WAT	7	Clear	Clear	7 - 8	6 - 8	4 - 6
Scher Bros. Scheroomid #1214	8	Clear Viscous	Clear	8 - 10	8 - 10	8
Proctor & Gamble ORVUS E.S. Paste	9	Clear	Clear	6 - 8	6 - 8	4 - 6
Witco CDA(1%)+P&G ORVUS(0.2%)	10	Cloudy	Clear	6 - 8	6 - 8	4 - 6
Feather Extract (Laur.Conc.)	11			6 - 8	6 - 8	6

Properties of Foams

Agent Number	Bubble Diameters in Cm. 1% Solution	1% Soln. + 2% DAP	1% Soln. + 2% MAP	Foam stabilities: ml of air per min. needed to make rate of foam formation equal rate of foam collapse 1% Soln.	1%+DAP(2%)	1%+MAP(2%)
1	11.5 / 15.2	16.4	13.1	5.0 / 5.5	6.4	14
2	14.3	-	-	2.8 / 4.0	8.2	-
3	7.6	6.8	7.5	3.5 / 4.6	4.2	5.4
4	19	15	15	4.5	4.7	4.1
5	16	-	-	9		
6	16	-	-	5	-	-
7	15	19	18	4	-	4
8	15	3	15	5	-	6
9	17	14	14	6	3	3
10	17	-	16	5	-	4
11	5	5	6	8	27	5

Properties of Foams

Agent Number	Foam Life Index: ml. of foam left after 5 min. ÷ original vol. of 2300 ml. 1% Soln.	1%+DAP(2%)	1%+MAP(2%)	Foaminess: ml. of foam standing above 10 ml. solution, 1 min. after shaking 1% Soln.	Soln.+DAP	Soln.+MAP	Additional Notes
1	0.14	0.22	0.09	47	41	41	
2	0.40	-	-	49	-	-	Max. bubble dia.(16.0) at 0.5% Apparently DAP raised foam stability.
3	0.47	0.24	0.20	43	42	44	Addn of DAP or MAP apparently does not hurt bubble strength or foaminess, but does stability and life.
4	0.35 / 0.22	0.16	0.25	54 / 46	42	44	Apparently phosphates do not harm.
5	No foam after 3'			67			Bubbles strong, but stability poor.
6	0.45	-	-	48	-	-	
7	0.30	0.33		59	62	54	
8	0.41	-	0.26	47	10	9	Retardant MAP OK for bubbles, but not life.
9	0.18	0.49	0.47	54	6	39	Retardant increased stability & life. MAP improved stability; didn't hurt life.
10	0.58	-	0.45	49	-	27	
11	0.10	0	0.21	44	27	28	

Under Foam Stabilities, in Table 3, the figures represent the air admission rates (for bubble inflation) in ml/second necessary to make the rate of foam equal to the rate of foam surface collapse. Thus, the lowest rates indicate the greatest stabilities. Only one of the agents tested equaled the performance of the first standard for comparison (JET-X). In several cases the addition of 2% concentrations of the phosphates did not significantly decrease the foam stability, and in one case (Agent Number 9) quite improved it! In the case of the second Comparison Standard (Agent Number 11) the diammonium phosphate addition decreased the foam stability very much.

Among the Foam Life Index data, Agents 2, 6 and 8 have values approaching that for Comparison Standard Agent 3. Mixed Agent Number 10 showed a value exceeding the value of the standard considerably. With 2% monoammonium phosphate inclusions, the foam life of Agents 9 and 10 was found to be twice that of Standards 3 and 11, with similar phosphate inclusions.

In Foaminess, all of the nine other agents exceeded the performances of both Standards 3 and 11. With 2% monoammonium phosphate inclusions, three of the other agents approximated the foaminess performance of Standard 3, and one showed considerably better performance.

Referring again to Comparison Standard Agent 3, and considering all five evaluation factors for each foam-forming liquid, Agents 4, 7 and 8 all seem to possess all five desired important properties in amounts comparable with those for these five properties of Agent 3.

SUMMARY

Three formulations for producing air inflated foams seem to have as good qualities as Comparison Standard Agent 3. The procedures developed for evaluation measurements of the properties of these foam stabilizing agents should be adequate for other compounds. Several interesting observations were made during Maximum Bubble Size measurements, which probably should be followed up later. For one of the foam formulations quite widely different bubble diameters at the time of bursting were obtained. The largest observed diameters were approximately twice the diameters of the smallest collapsing bubbles observed. In another case, there appeared to be a multiple of 3. Whether this was a chance occurrence, or whether a characteristic performance, could not be determined at this time. If the occurrence is characteristic, perhaps the explanation may involve phenomena in bubble wall composition -- perhaps even the existence of multiple-thickness layers of oriented stabilizer-molecules at the liquid-air interface. Also during the Maximum Bubble Size measurements, two further interesting trends were noted, related linearly to the logarithm of the concentration of the stabilizing agent. For Foaming Agent 29, and also for Witco Ultrapole CDA, there seem to exist 'critical' concentration values, at thich the bubble size reaches a maximum value.
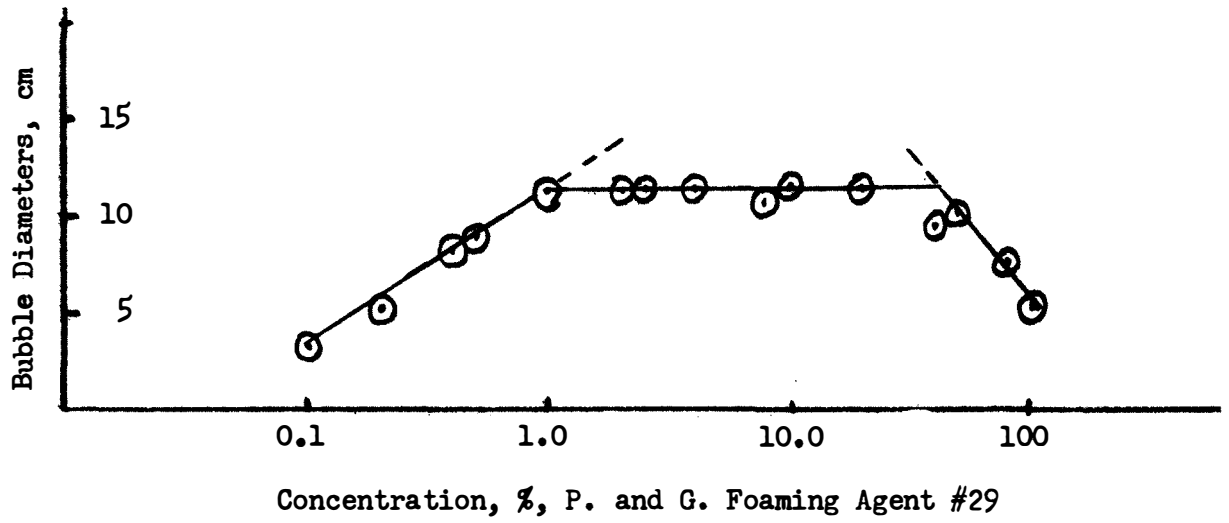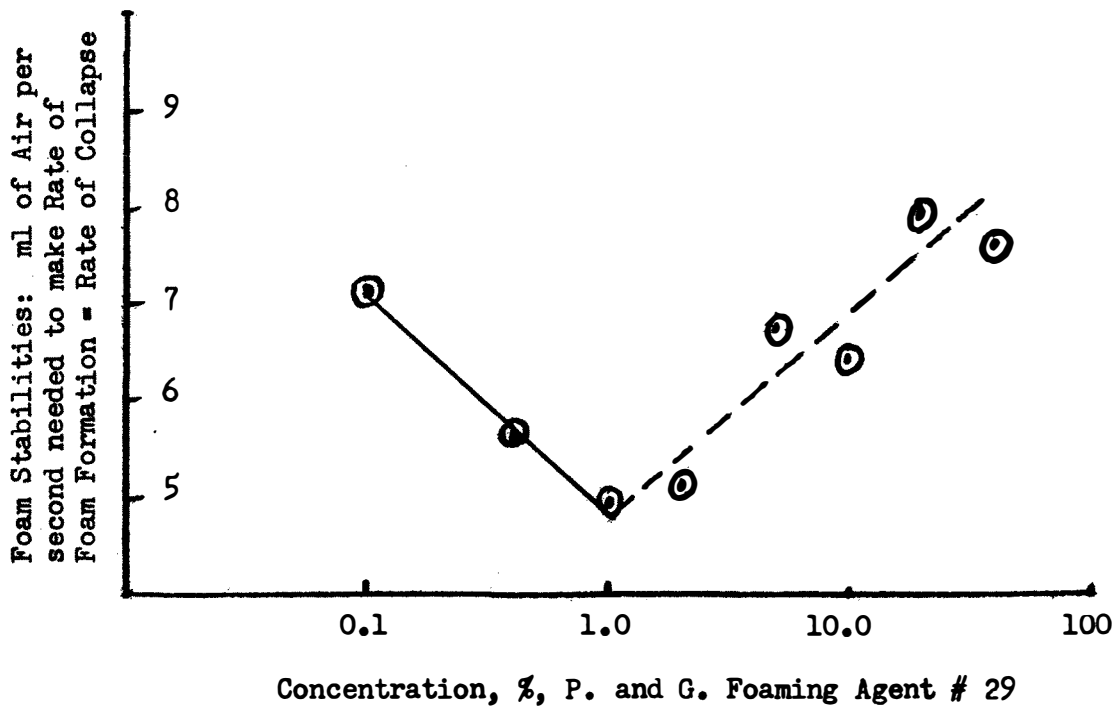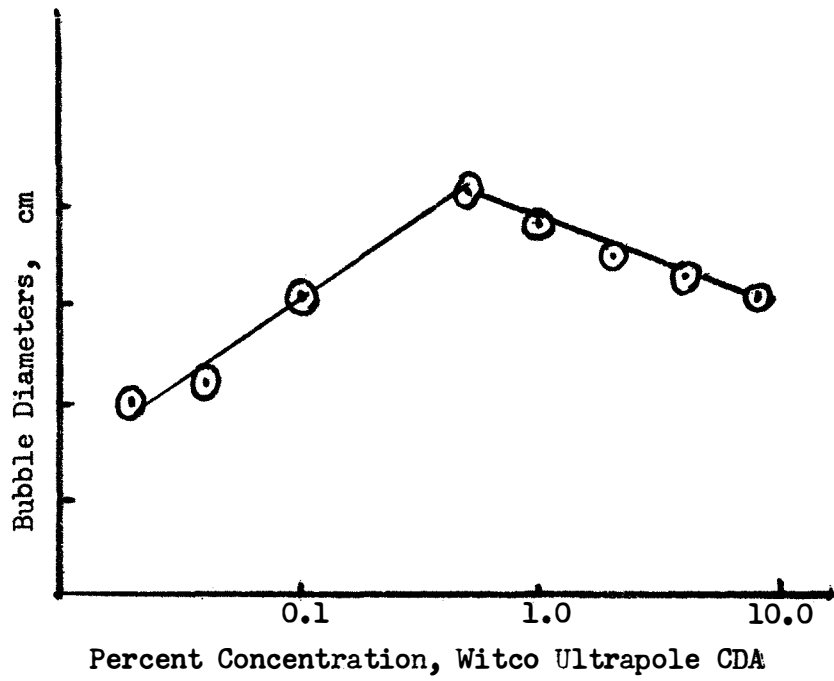
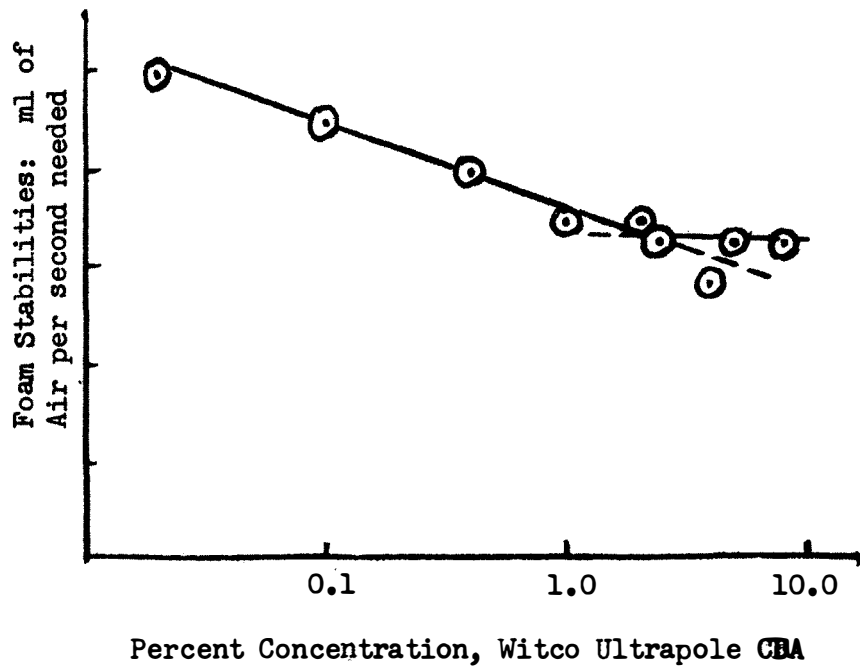Figure 5

Figure 6

Figure 7

Figure 8

At concentrations below this, the bubble diameters decreased noticeably (see Figures 5 and 7) with decreased concentration of agents. In runs represented in Figure 9, with JET-X, apparently the critical concentration value was never reached. For Proctor & Gamble Foaming Agent 1 (Figure 5), and for Witco Ultrapole CDA (Figure 7), the critical concentrations appeared to be in the region of 1%.

While the maximum bubble size dropped rapidly for concentrations greater than the critical one in the case of the Ultrapole CDA, the same maximum bubble size for the Proctor & Gamble Foaming Agent 1 persisted over a concentration range of from 1% to about 40%, and then decreased. Agent 29 is non-ionic.

Foam stability values obtained with solutions or dispersions of Agent 29 (Figure 6) and of JET-X (Figure 10) also seem to indicate the existence of 'critical' concentration values for foam stabilities which seem to occur in the region of 1% concentrations.

The fact that both maximum bubble sizes and foam stabilities appear to be linear functions of the concentrations of the foam stabilizing agent would indicate an interesting relationship between the maximum bubble size and the foam stability. From the left hand parts of Figures 5 and 6, and 7 and 8, perhaps one might rationalize that foams with strong bubble walls tend to survive longer before collapse. More measurements are needed certainly, especially for Ultrapole CDA foam stabilities (Figure 8) in order to draw any definite conclusions along this line. Experimental data are given in Tables 4, 5 and 6, for the water solutions or dispersions of Proctor & Gamble Foaming Agent 1, Witco Ultrapole CDA, and JET-X Foam Fluid. Data from these tables are shown in Figures 5 through 10, already referred to.

Table 4. Properties of water-diluted
Proctor & Gamble Foaming Agent

Concentration %	Average-maximum bubble diameters	Foam stability data, ml/sec
0.1	3.4	7.2
0.2	5.3	–
0.4	8.3	5.7
0.5	9.0	–
1.0	11.2	5.0
2.0	11.3	5.2
2.5	11.6	–
4.0	11.5	–
5.0	–	6.8
8.0	10.9	–
10.0	11.8	6.5
20.0	11.8	8.0
40.0	9.7	7.7
50.0	10.3	–
80.0	7.9	–
100.0	5.4	–

Table 5. Properties of water-diluted
Witco Ultrapole   CDA

Concentration %	Average-maximum bubble diameters	Foam stability data, ml/sec
0.02	5.0	5.0
0.04	5.20	-
0.1	10.5	4.5
0.4	-	4.0
0.5	16.0	-
1.0	14.3	3.5
2.0	12.8	3.5
2.5	-	3.3
4.0	11.6	2.9
5.0	-	3.3
8.0	10.8	3.3

Table 6. Properties of water-diluted
JET-X   Foam Liquid

Concentration %	Average-maximum bubble diameters, cm	Foam stability data, ml/sec
0.1	2.4	5.4
0.4	-	4.1
0.5	4.1	-
1.0	7.0	2.5
2.0	8.8	2.5
4.0	10.3	3.7
10.0	13.0	4.8

FURTHER WORK INDICATED

While five of the Agents listed above (including Comparison Standard Agents 3 and 11) produce good foams, their foam stabilities all fall short of the goal of a foam which will last for at least half an hour.

Only one agent known to be non-ionic was tested (Proctor & Gamble Foaming Agent), and no cationic ones, several agents of each type (anionic, cationic, non-ionic) should be tried in order to determine on which type further evaluations should be made. A number of samples of foaming agents and stabilizers reached the Station after the writer had concluded his work and returned to Florida. These have not yet been evaluated.
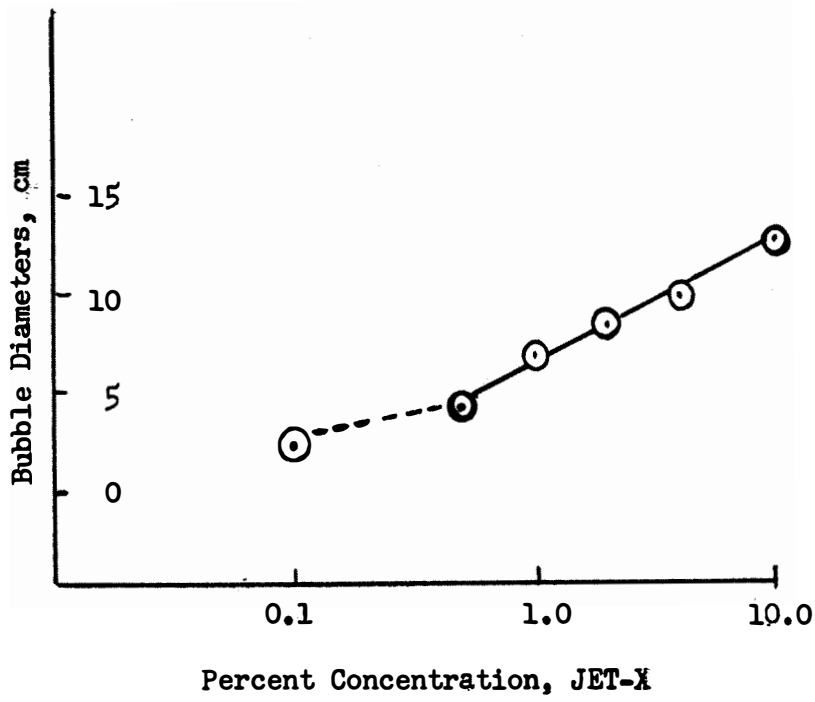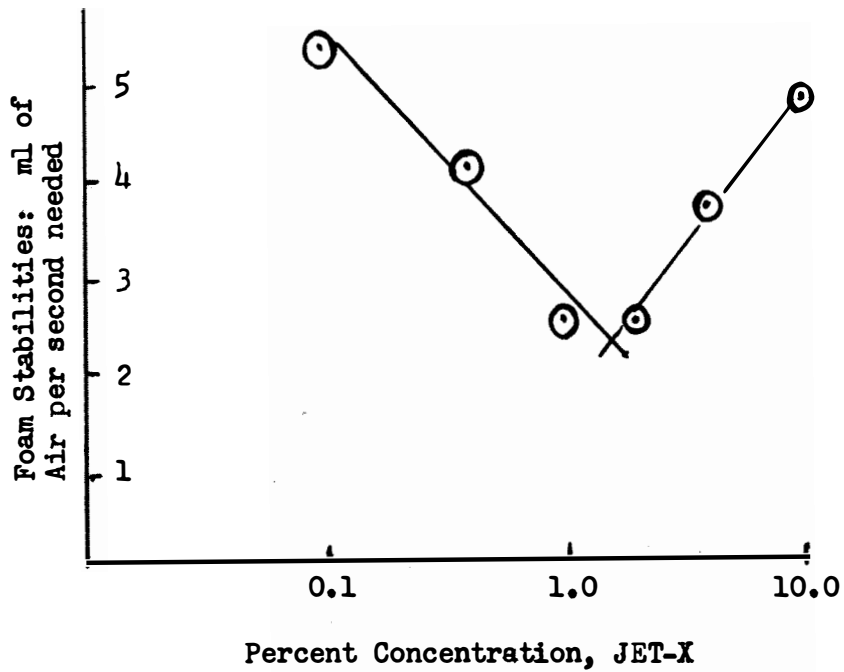
Figure 9

Figure 10

Results obtained with the tenth agent listed in Table 3 (a blend of two agents) indicate that further trials should be made with pairs of foam stabilizers. In a publication more than 20 years ago, Miles and Ross noted the advantages of using mixtures of 2 foam stabilizers. Pairs of stabilizers should be chosen with some theoretical basis. It would seem logical to try pairs of agents which promote foam-forming and foam stability for quite different reasons, for example, a pair comprising one anionic foam stabilizer combined with a non-ionic stabilizer, an anionic foam stabilizer combined with a protein-type stabilizer (perhaps gelatin), an anionic stabilizer combined with a pectin or carboxymethyl cellulose viscosity-building agent, a non-ionic stabilizer combined with a viscosity-building agent, etc.

It would be advantageous to carry on studies to extend the field of theoretical knowledge about foam formation. These should include studies of the relations between surface tension lowering and foam-forming ability. More should be known about possible relations between surface tension and foam life, possible relations between solution viscosity and foam life, and especially the possibility of greatly increasing foam life by combining a suitable foam stabilizer with carboxymethyl cellulose to which aluminum salts have been added to form semi-solid walls in foam bubbles. An extended study of the indicated relationship between maximum bubble size and the foam stability might be rewarding, and it would be interesting to see if maximum bubble size is related to the foaminess.

In summary, there are several categories of further work indicated, including:

(a) the continuation of routine exploratory evaluation of single, and later paired, foam-forming agents of different types (anionic, cationic, non-ionic) in the hope of finding one (or one pair) which is outstandingly good;

(b) additions of selected gel-forming agents to foam-forming agent solutions — to increase the foam life appreciably;

(c) somewhat theoretical studies in surface chemistry (physical chemistry of foams) to discover new guidelines in the search for new formulae for the production of stable, strong foams containing about 2% concentrations of fire-retarding mono-ammonium phosphate.