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FOAMING OF AIRCRAFT-ENGINE OILS AS
A PROBLEM IN COLLOID CHEMISTRY - I

By J. W. McBain, S. Ross, A. P. Brady, J. V. Robinson,
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ADVANCE RESTRICTED REPORT

FOAMING OF AIRCRAFT-ENGINE OILS AS

A PROBLEM IN COLLOID CHEMISTRY - I

By J. W. McBain, S. Ross, A. P. Brady, J. V. Robinson,
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SUMMARY

An investigation has been conducted on the foaming characteristics of representative aircraft-engine lubricants in order to arrive at an adequate theory of the foaming of such oils. In the course of the research the effect of adding a large number of chemical agents was studied, and the results of these tests are presented.

Methods of measuring foaming have been compared and analyzed for their significant factors.

While it was not possible to establish a relationship between chemical composition and the foaming tendency of aircraft-engine lubricants in the preliminary investigation, which is described in this report, considerable progress has been made toward the goal. In addition, many antifoaming agents have been tested which, in laboratory tests, are adequate to prevent or minimize foaming of aeronautical oils. Certain of these agents are found to be ineffective at elevated temperatures.

Various theories on the foaming of chemical mixtures are discussed and developed, together with explanations of the action of antifoaming agents.

INTRODUCTION

The primary object of this investigation is to arrive at an adequate theory of foaming of aircraft-engine oils, enabling the producers of petroleum products to control manufacturing processes in such a way as to obtain lubricants which, by their nature, would not be subject to the foaming and aeration problems that now are being encountered in flight. In order to obtain specific information on the behavior of various chemical compounds, tests were made on the antifoaming effectiveness of a large number of hydrocarbons and other materials in representative aeronautical oils. The results of these tests, including experimental data and much of the discussion on foam meters, theories of foaming, and other phases of the investigation, are contained in a series of seven appendixes to this report.

This investigation, conducted at Stanford University on the chemical aspects of the foaming of aircraft-engine lubricants was sponsored by, and conducted with financial assistance from, the National Advisory Committee for Aeronautics.

STATEMENT OF PROBLEM

In normal operation, the oil-circulating systems of aircraft engines contain much entrapped air. This is admitted to the system by the excess capacity of the scavenge pumps, or by other mechanisms, such as agitation of oil in the crankcase, or in the tank as a result of an open jet impinging on the surface of the oil. If air is not prevented from accumulating in various parts of the oil-circulating system, it may displace oil from the system, cause improper functioning of both the scavenge and oil pressure pumps with resulting loss in pressure at the engine bearings, reduce oil flow to the engine bearings, and possibly enhance oxidation of the oil.

These various conditions are aggravated by altitude, since the atmospheric pressure head at the scavenge and pressure pump inlets is reduced, with a resulting loss in pump performance. Furthermore, air and other gases which normally are dissolved or suspended in the oil are liberated as bubbles during operation at altitude. Water, gasoline, and other volatile liquids that are present in

engine oil are more readily vaporized at the low atmospheric pressures which are obtained at altitude.

It would appear with existing oils that any airplane engine installation will meet with foaming difficulties to varying degrees if the system is operated at a sufficiently high altitude. It is obvious that any improvement that can be made in the oil from the standpoint of reducing the stability of foams that are produced by the above causes will raise, effectively, the altitude at which foaming and deleterious aeration otherwise would be present.

While this study of foaming and aeration was directed primarily at the chemical aspects of the problem, various tests that were made in the course of the investigation clearly indicate the necessity for providing a mechanical design in the airplane so that entrained air is permitted to rise to a free surface and thereby separate from the oil. This point is extremely important since no chemical foam-breaking agent will be completely effective until air bubbles are present at a free surface.

Certain features of mechanical design can be directly harmful if they tend to subdivide the entrained air and "emulsify" it in the oil, thereby intensifying the aeration problem. Such features are constrictions to the flow, viscosity valves, unsuitably designed pumps, and other devices that introduce turbulence into the oil stream.

It has been found that the chemical or colloid surface treatment not only is capable of eliminating free foam, but it also is effective in promoting segregation of the air by causing entrained bubbles to coalesce. Although it is true that an air bubble, as long as it is completely surrounded by oil, cannot collapse no matter how unstable it is, adjacent submerged bubbles if made unstable will coalesce to form larger submerged bubbles. These larger bubbles are more readily disentrained from the oil and in this manner the separation of air from oil is materially assisted. Hence, for these two reasons it is desirable to reduce the stability of air bubbles in oil by chemical treatment, or by removing from the lubricant the agent or agents that tend to increase the stability of air bubbles.

It is, therefore, obvious that the ideal solution to the foaming and aeration problem lies in the use of suitable mechanical design of oil-circulating systems together with a lubricating medium that forms air bubbles of minimum stability.

If the instability of entrained air bubbles is to be obtained by the use of an antifoaming agent, it is mandatory that such agent meet the following requirements:

- (a) It must be effective and compatible with all aircraft-engine lubricants that will be used in military and civil aviation.
- (b) It must be tested fully and approved by laboratory tests, including engine tests.
- (c) It must be thoroughly investigated in service-flight tests.
- (d) It must in no way impair the lubricating and stability characteristics of present aeronautical oils, either in storage or in service.
- (e) It must permit the aircraft-engine lubricants to pass all existing specified tests.
- (f) It must be available in quantity and must be of such nature as to be definitely specifiable in regard to composition and purity.

ANALYSIS

The investigation of the foaming characteristics of aircraft-engine lubricants was broken down into several classifications, and a complete description of the research conducted under each heading is given in the following appendixes to this report:

- Appendix I - Theories of foams, films, and antifoaming agents
- II - Methods of measuring foam
- III - Characteristics of existing lubricating oils
- IV - Survey of the effects of chemical agents on oil foaming
- V - Known mixtures of pure chemicals as foam inhibitors

VI - The inhibition of foaming in a series of solvents containing known foamers

VII - Attempts to remove foaming agents from lubricating oil

The following paragraphs give a brief discussion of the results obtained in each phase of this investigation.

Theories of Foams, Films, and Antifoaming Agents

Appendix I presents a discussion of several theories that have been advanced at various times on the foaming characteristics of aqueous and nonaqueous solutions. Particular emphasis is given to those theories which are applicable to aeronautical oils.

A study of the literature indicates that there is little published information concerning foaming and defoaming of nonaqueous liquids. The balanced layer theory of Foulk and Miller, Hardy's suggestion regarding the oriented, adsorbed monolayer, the plastic solid surface theory of Wilson and Ries, the theory of solvation of the adsorbed monolayer by Talmud, and the theory advanced by Hardy and McBain on oriented molecular chains extending inward from surface films, are discussed in the light of their application to aeronautical oils. Several of the more probable theories are expanded somewhat, and experimental data are quoted where available. It is shown that there is no accepted experimentally established theory on the foaming of aircraft-engine lubricants or even of aqueous liquids. Inhomogeneity of a film is frequently, but not always, an effective cause of breaking foam.

Methods of Measuring Foam

Information is given in appendix II on several methods that were investigated for producing foam and for determining the relative stability of foam formed by aircraft lubricating oils.

Different techniques of foam measurement are discussed in some detail, and suggested methods for numerically defining the stability of foams are presented.

Three rapid methods for investigating foam inhibition also are given. They consist of the film break or "pop"

test, the measurement of liquid film stability by a "ring" test, and a study of the stability of single bubbles. Comparative data are given on results obtained by these three tests together with pertinent comments on the range of usefulness of each method.

Characteristics of Existing Lubricating Oils

In this study it became desirable to determine the foam formation and the stability characteristics of present-day aeronautical lubricating oils by various methods of foam-testing. The foam stability of several new and used oils was measured at room temperature and at 100° C. In many cases intermediate and higher temperatures also were studied. This information is given in appendix III.

It was found that, in general, there is a decrease in foam stability with rising temperature. Some exceptions to this were noted and are described.

An attempt was made to correlate physical properties of lubricants with the foaming tendency and foam stability, and there is evidence to indicate that kinematic viscosity is one of the primary factors involved. Chemical analyses of certain typical new and used aeronautical oils are included.

Survey of the Effects of Chemical Agents on Oil-Foaming

Because of the lack of adequate theories for the relationship between chemical composition and foaming tendencies of aqueous and nonaqueous solutions, an empirical study was made on the antifoaming effectiveness of a large number of pure chemicals and commercial compositions added to normal oils. This study, which is reported in appendix IV, was made over a range of temperatures and concentrations of additives, and in many cases several methods of test were used. The presence of water also was investigated and was found in many cases to have a controlling influence on the antifoaming effectiveness of certain agents.

The results of foaming tests on hundreds of different materials and chemicals in oil are presented in tabular form.

Known Mixtures of Pure Chemicals as Foam Inhibitors

The research reported in appendix IV was expanded further in an attempt to evaluate the effect of chemical inhomogeneity in the film as a mechanism for reducing film stability. The experimental evidence contained in appendix V lends support to this theory.

Test data are given on the effect of a series of mixtures which were prepared in accordance with this hypothesis. Suggestions are included regarding certain compounded agents which are effective in greatly decreasing the stability of foams in aeronautical oils.

The Inhibition of Foaming in a Series of Solvents Containing known Foamers

Appendix VI contains the results of a series of experiments which were made to determine the effect of incorporating various known agents in several well-defined chemical systems that were capable of forming foam. Two types of solvent were studied. The first was a series of water-miscible liquids and the other a white mineral oil. It was noted that in many cases the defoamers were relatively insoluble, and that the effect of concentration was marked, particularly when materials of lower solubility were used.

Comparative tests on the bulk-foaming characteristics of a defoaming agent with the action of the additive on a single film show excellent correlation. The spreading of additives on single films is discussed from various viewpoints.

Attempts to Remove Foaming Agents from Lubricating Oil

Appendix VII describes the results of a brief series of tests that were made to determine the practicability of removing foam-causing agents from normal lubricating oils on the theory that such oils as produced contain certain materials which act as foaming agents. The research indicated that there is definite promise in this method of attack, and further research is contemplated.

CONCLUSIONS

As a result of the research described in the seven appendixes to this report, the following conclusions may be drawn:

1. At present there is no adequate theory on the foaming of aircraft-engine lubricants. Since it is known that pure liquids do not foam, it is believed that there is a sufficient quantity of foaming agents of unknown character existing in aeronautical oils to cause mild foaming. This mild foaming tendency will lead to a severe aeration problem when aggravated by adverse mechanical conditions in an aircraft-engine oil-circulating system.
2. A number of antifoaming agents have been investigated which are adequate to prevent or minimize the foaming of aeronautical oils, especially at room temperature. Several of these agents are less effective at temperatures approximating the highest temperatures found in current aircraft-engine oil systems.
3. Tests of a series of solvents and a series of foaming agents indicate that there is no universal foaming agent and no universal antifoaming agent. The foaming agent and its antidote are fairly specific, but may be the same for a series of solvents that are generally similar.
4. The stability of foam produced by moderately foaming liquids, such as normal aircraft-engine lubricants, depends greatly upon the manner in which the foam is produced and the environment.
5. The average lifetime of an air-supported film in normal aircraft-engine oils is found to vary between the approximate limits of 3 seconds and 1 hour. It is possible to add to the oils antifoaming agents that will cause every exposed film to collapse instantaneously, with the result that there can be no foam formation at a free surface. The effectiveness of certain antifoaming agents depends greatly upon the method of introduction into the lubricant.
6. Some antifoaming agents become inoperative under imperfectly understood conditions of temperature, moisture, concentration, and use. However, nearly all the antifoaming agents that are effective at high temperature retain their effectiveness at lower temperatures.

7. Methods of test have been developed which permit a rapid survey of the effectiveness of experimental foaming agents and antifoaming agents.

8. Heterogeneity of a bubble film is apparently the most effective cause of breakage. As a result, mixtures of two pure chemicals, an alkyl succinyl sodium sulfonate and glycerine, form an especially effective antifoaming agent.

Stanford University,
Stanford University, Calif., May 1944.

APPENDIX I

THEORIES OF FOAM, FILMS, AND ANTIFOAMING AGENTS

Definition

A foam is a heterogeneous system, consisting of a dispersed gas phase, separated by films of a continuous liquid phase. For this system to appear stable, the continuous liquid phase must resist the forces of gravity and capillarity and maintain itself in the films.

With aqueous solutions liquid films have been produced of such stability that they will last in a protected environment for months at a time (reference 1). Likewise, certain foams containing many such films may be preserved indefinitely. There are foams of all intermediate stabilities down to the other extreme of pure liquids which do not form "foams," in the sense used above, at all.

Pure Liquids

It has long been stated that pure liquids do not foam. A few cases have been cited in the literature in contradiction to this statement. In such cases criticism has been made of the experimental technique on the grounds that the liquids examined were not pure. In this laboratory a number of liquids of various chemical types have been examined and in no case was it found that any of the liquids tested would foam, or even form occasional bubbles of more than 2 seconds duration. These tests in most cases were conducted at room temperature by merely shaking the bottle. In a few cases the liquid was tested by forming single bubbles with a medicine dropper, the surface-swept sample being held in a watch glass. Following is a list of the materials examined. Those with an asterisk are solid at room temperature and were tested at 10° to 20° C above their melting points. All other materials were examined at room temperature.

Di-stearone*	Butyric acid
Di-cetyl*	Oleic acid
Diethylene glycol	Isohexane
Methanol	n-Butyl phosphate
Ethanol	Tributyl phosphate
Acetone	d-Limonene
11-Decyl hexacosane	2-Ethyl hexoic acid
Toluene	7-Ethyl, 2-methyl undecanol 4

C. G. Lindquist examined the hydrodynamic drainage of liquid films, on the assumption that the liquid was truly fluid or Newtonian. The details and the calculations are not repeated here, but the conclusion is drawn that for bubbles of completely mobile surface and in the range of viscosity of lubricating oils bubbles must thin down to molecular dimensions and break within about 1 second. This presents a reason pure liquids do not form froth. On the other hand, if the actual surface were completely rigid, the oil film would require the immense period of 10^{12} to 10^{13} seconds to thin down to 10 \AA .

Actually, oils produce films which have a moderate lifetime. Hence since their surfaces are mobile, or possess no yield value, there must be a structure extending within the liquid to hinder free drainage, or else the surface itself or the surface zone must possess some plasticity. Plateau (reference 2) would have grouped these two hypotheses together, using the term "surface viscosity." The evidence that is accumulating in the observations at Stanford University supports the former alternative without excluding the demonstrable occurrence of the latter in cases of aeronautical oils containing certain foaming additives.

It is possible to discriminate between three conceptions, of which the first is apparently not applicable in the case of aeronautical oils; whereas the second appears to be general for them; and the third represents an additional factor when certain foaming additives are added and conceptions (b) and (c) both apply.

- (a) A rigid monomolecular film, such as a saturated fatty acid or water
- (b) A surface where the effects of orientation extend inward to an appreciable depth within the oil
- (c) A thick, multilayered or gelled plastic film upon the surface

Theories of Foam

Hitherto, discussion of the phenomena and the explanation of foams have been concerned with aqueous systems. The following suggestions condensed from the literature were originated for aqueous systems.

The balanced layer theory (reference 3).— Liquid films always are formed by the approach to each other of two already formed liquid surfaces (e.g., two bubbles coming together or a bubble rising to a surface), usually with an extension of area. The forces preventing merging of the surfaces and destruction of the film arise from the differences in concentration between the surface and the bulk of the liquid. This difference is an equilibrium condition and therefore will resist forces tending to eliminate it. It would be well to generalize Foulk's theory, pointing out that any difference between the bulk and the surface zone of a liquid that is spontaneously produced must require work to eliminate it again, and hence any such difference will confer foam stability. A difference between dynamic and static surface tension was Foulk's criterion for a difference between surface and mass concentration. Hence, it was supposed that the solutions making the most stable foams would be those showing the greatest difference between static and dynamic surface tension. Foulk's experimental corroboration has been subjected to severe criticism on the grounds of inaccuracy. Because of the difficulty of obtaining dynamic surface tensions, there is little other experimental evidence. The theory is quite unsatisfactory in furnishing an explicit mechanism, but supplements the idea of film stabilization due to sorption. Antifoaming corollaries to the theory are discussed in a later section.

Oriented adsorbed monolayer.— A more explicit theory than that of Foulk was given by Hardy prior to that of Foulk, and not restricted by the uncertainty of the surface-tension concept.

A sharp maximum in film stability, measured by the life of single bubbles, occurs when the surface concentration of a floating insoluble film on water corresponds to a monolayer about one-third saturated — that is, a monolayer in the condensed phase, but not highly compressed (reference 4). For a foaming system in which the foaming agent is in solution, this theory would require positive adsorption of the agent at the surface, and in a concentration corresponding to unsaturated monolayer, as with the insoluble film.

Experiments on aqueous foaming systems (references 5, 6, 7, and 8) have shown that the foaming agent is adsorbed in the films, in concentration of the order of magnitude of a monolayer. The experiments of Harkins (reference 5) show the adsorption to correspond approximately to a partially

saturated monolayer, as found by Hardy to have the maximum stability. A qualitatively similar concentration of the foaming agent has been found with aviation oils containing an additive (appendix V).

The experiments cited on aqueous foams showed that the adsorbed layer is formed on both sides of the liquid film in the foam, thereby forming a sort of sandwich of liquid between two surface layers. Hardy demonstrated that with a thick film of water between monomolecular layers of oleic acid, the surfaces were comparatively immobile, while the center film was liquid and flowed under the influence of an electric field.

The plastic solid surface theory (reference 9).— Wilson and Ries extended the idea of a rigid surface layer beyond the concept of monolayers, to sorbed layers of great thickness (0.001 to 0.004 cm) having the properties of plastic solids.

To account for the ability of certain liquid films to resist for an indefinite period the forces of gravity and capillarity tending to thin them, it may be assumed that the walls of the bubble or film possess the properties of a plastic solid rather than of a liquid. Wilson and Ries have shown that certain aqueous soap solutions show the viscosity characteristics of a plastic solid in a thin region at the surface of the solution. This plastic surface developed when a certain bulk concentration of solution was exceeded, the point varying for different soaps. These authors correlated the formation of the plastic solid surface with foaming ability, by shaking the solutions in test tubes.

By precipitating colloidal barium sulfate in the soap solution, they were able to note the process of "solidification" of the surface, using an ultramicroscope focused on the surface and observing the Brownian movement. A short time after the disturbed surface became quiet, Brownian movement in the surface layer ceased. The focus of the microscope was then lowered to the next layer where Brownian vibration of the barium sulfate was visible, and after a short time that, too, ceased. A sharp shock would restore the vibration for a time. The greatest depth of this immobile layer varied from 0.001 to 0.004 centimeter. Wilson and Ries noted that in the immobilized layer, the particles all vibrated together as though in a jelly.

The degree of hydration of the adsorbed monolayer (reference 10).— Talmud combines the oriented monolayer ideas and experiments of Hardy with the deep surface of Wilson and Ries and describes in detail a model of such a surface, in which the depth of surface arises from hydration of the monolayer.

Talmud supposes that the tenacity of an adsorbed film depends upon the degree of hydration of its polar groups. The degree of hydration, in turn, depends upon the orientation of the molecules sorbed at the surface, which is governed by the packing, or surface concentration. When the surface is about one-half saturated, the maximum hydration occurs, since, when the molecules are less packed, they lie flat on the surface and the nonpolar chains interfere with the hydration of the polar groups; when the molecules are closely packed, all water is squeezed out from between the chains. In the neighborhood of the maximum hydration of the polar groups, the molecules of the surface active substance interlock with each other to form a hydrated structure resembling a gel.

When an air bubble rises beneath an insoluble surface layer of this type, it will be most stable when the layer is most hydrated, owing to the gellike structure. When the layer is packed to a greater or lesser extent, it is less hydrated and fluid in character, and the bubble bursts.

When an air bubble rises through a solution of soluble surface active agent, beneath a surface on which the agent is sorbed, the maximum bubble stability will occur at a lower concentration than that corresponding to maximum hydration of the surface layer. In this case, there also will be a sorbed film on the bubble surface, so that at the point of contact of the bubble with the surface there will be a greater concentration of sorbed material. If the concentration is that at which greatest hydration of the sorbed layer occurs, the point of contact of bubble and surface films will be more closely packed and therefore less hydrated, and the bubble will burst. (An error in this part of the theory may here be pointed out. As described, the surface on the inside of the bubble and the liquid surface are treated as having no thickness, so that when they come together, they merge. Actually this is impossible, because the two surfaces must be separated as long as any film exists. The layer on one is oriented in the reverse direction to the layer on the other, so the two layers may at closest approach only touch, and cannot be telescoped one into the other to produce a net concentration equal to the sum of the two.)

The degree of hydration of the sorbed layer affects the drainage from the film surrounding a bubble of air in a foam. Drainage is greater under a close-packed insoluble film and less under a heavily hydrated film in which the surface has great depth. Long chain insoluble substances give relatively "strong" adsorption layers, but not stability; whereas short chain soluble substances give great stability in spite of "weak" adsorption layers. The slow drainage in the latter case is due to the thicker gel structure. The smaller stability of an insoluble layer is due to rapid drainage between the less hydrated layers.

In his experiments, Talmud finds that if the solvent evaporates, single bubble stability increases, and if the solute evaporates, stability decreases.

A "solvation" theory such as this becomes somewhat more complex when applied to nonaqueous systems. In a hydrocarbon system, for example, the polar groups of a sorbed layer at an air surface would be toward the air rather than toward the liquid. The formation of a hydrocarbon gel bound by the nonpolar chains is conceivable, although little is known as to its occurrence.

The opposition of similarly charged surfaces, and the theory of oriented chains extending inward from surfaces.— All surfaces are charged, even those of nonconducting liquids. Most systems are neutral because of the presence of an equal number of opposite charges, but their unequal distribution leads to a potential difference at the surface. A film of foam represents two such charged surfaces separated by liquid.

A great deal of somewhat inconclusive work has been done in aqueous systems on the apparent difficulty of bringing together in water surfaces of similar charge. The point is that each such surface holds within the aqueous layer an equal number of ions of sign opposite to that of the surface. Some of these ions are sessile or in close contact with the charged surface, as in the original conception of the Helmholtz double layer. Others are free and mobile in the diffuse part of the double layer first suggested by Gouy in 1910 and now universally accepted as a part of the "ionic atmosphere" of any charge in an ionizing solvent, according to the Debye-Huckel theory or the principle of the Donnan equilibrium. In water, at sufficiently low concentration of salts the diffuse double layer may extend to a distance of 10,000 Å or more from a charged surface.

Many observers maintain that surfaces of colloidal particles have been found at an equilibrium distance varying from 200 to 70,000 Å from each other. The Dutch school, led by Hamaker and Freundlich, considered that the electrical forces were repulsive and kept the surfaces apart while a long-range attraction was maintained at a distance where the electrical repulsion was disappearing. However, several writers, such as Porter, Langmuir, and others, have pointed out the obvious consideration that in a condenser such as is provided by two charged surfaces with an equal and opposite charge placed between them, the electrical force is one of attraction and some other force must be suggested for keeping them apart. The very fact that salts freely ionize in water, and that diffuse layers spontaneously form, shows that there is a mechanism of keeping opposite charges apart. This McBain ascribes to two factors. First, the thermal vibrations or Brownian movement of ions and solvent molecules alike, which tends to make them diffuse among each other in spite of a one-sided attraction. Second, the chain mechanism or relayed orientation, suggested independently in 1927 by McBain (reference 6) and Sir William Hardy (reference 11). A surface, in its strong orienting power is like a magnet which can orient long chains of iron particles, as long as the first one remains in contact with the magnet. Thus oriented chains of solute and chains of oriented polar solvent molecules must extend into the liquid from any surface. The positive thrust or displacement so occasioned will keep the diffuse layer deep. Such orientation must be at least equally prominent in nonionizing systems where there is no diffuse double layer. It will be especially marked with long chain molecules which have a strong tendency toward association or cybotaxis. It has been shown by Clark (reference 12) in the United States, Tausz (reference 13) in Germany, and Trillat (reference 14) in France, that in lubricating oils such oriented layers extend to the order of 10,000 Å into the liquid from a metallic surface. Likewise, the experiments of Beeck (reference 15) and others on "wedging" and similar effects in lubrication show that orientation of molecules of dissolved substances extends inward from the surfaces of lubricating oils. This theory is therefore of the most direct interest in the study of aeronautical lubricating oils.

Foam theories considered in relation to the foaming of aviation oils.— The theories presented are similar in that all depend upon adsorption at the air-liquid interface; all except that of Foulk require positive adsorption. The theories

differ principally in the supposed thickness of the sorbed layer. Talmud gives a mechanism for the formation of thick films in aqueous systems. McBain (reference 6) explains thick films by the theory of oriented chains extending inward from surfaces.

Sorption at the film surfaces has been demonstrated for an aviation oil in which an additive was dissolved (appendix VII). The additive concentration was greater in the liquid from collapsed foam than in the original. However, an aviation oil not containing an additive foams markedly, and may be foamed completely away without any detectable difference in composition (by interferometer analysis) between the liquids obtained by collapse of different portions of the foam. Furthermore, a white mineral oil (Nujol or Squibb's), presumably containing only hydrocarbons, also foams, as do synthetically produced polyolefins and polyisobutylene. Additives which are successful defoamers for the undoped aviation oils and white oils are not equally good defoamers for aviation oil with an additive already in it. Further elaboration and extension of any of the theories given is necessary to cover these cases.

Surface structure of considerable strength has been demonstrated for pure liquids at an air-liquid interface (reference 16). If a pure liquid can form such a structure at its surface that a drop of the same liquid will not break through the surface, but will roll around on top for some seconds, it seems reasonable to suppose that a mineral oil, with a variety of hydrocarbons in its composition, could by some mechanism form a similar surface structure. If such were the case, it is not surprising that any change in composition at the surface would resist detection by usual or simple means. If this can be shown, then, in conjunction with the demonstrated stabilization of foam by sorption in the case of an oil containing an additive, the basis for a consistent theory has been established.

The question of film thickness in a stable foam is of the utmost importance. In a column of foam from an aviation oil in a glass tube, stable for many minutes or even hours, interference colors can be seen on the individual films.

"Black" films would have to be about 125 \AA thick (reference 17); "gray" films, from 125 to approximately 1200 \AA thick. Therefore, the actual films are very many molecules thick, and the effect of the surfaces must be sufficient to immobilize a body of fluid comparatively far removed from the

surface. Any complete theory of foams must, therefore, include some mechanism to explain the existence of a deep structure.

Further evidence for the thick structure of certain films is that they spontaneously break without seeming to drain to extreme thinness. The foam of an aviation oil containing an additive was "white" after 30 hours at room temperature. This cannot be ascribed to high viscosity of the oil in bulk, but rather would seem to indicate a thick immobilized layer due to enhanced viscosity in the surface zone. Aviation oils not containing an additive similarly have never been seen to reach the black thickness, although periods of drainage of more than a few minutes have usually not been possible.

Talmud, in describing the rapid breaking of films with strong adsorbed layers of long chain substances, also implies the spontaneous breaking of fairly thick films. The pop test demonstrates that it is possible to disrupt explosively a very thick film, or even a lens, without mechanical shock, by applying minute traces of certain agents to it. Hardy (reference 18) similarly suggests that drainage is not an essential mechanism for the spontaneous rupture of a film. In considering an explanation for the maximum stability of a bubble released under a surface covered by a certain thickness of oleic acid, Hardy suggests that the mechanical stability of the film falls as its two sides become less symmetrical, owing to the increasing difference in the density of the water faces. The water in the middle is modified throughout by the interfaces; and when these are dissimilar, it is like an unannealed plate; that is, it simply fractures.

Thick Films Obtained with Certain Additives

During the course of this investigation of lubricating oils, foams of considerable stability have been observed on numerous occasions. A "stable" oil foam in a vertical cylinder collapses in either of two ways. First, the foam structure may remain practically intact while the oil slowly drains from the topmost layers. Thus, after an hour or more, the topmost layers are a very pale yellow; these films may be described as "thick." The bottom part of the column of foam has a brownish yellow color and may be described as "very thick." The second type is one which begins to collapse at a "normal" rate and then slows up with the formation of "macroscopically thick" immobile films one of which

may extend across the entire cross section of the cylinder (about 3 cm diam.). These films, because of their extreme durability and longevity, are of particular interest. Less attention was given to the slow, steady foam collapse; although the drainage is very much slower than normal.

The formation of both types of thick oil film has been observed only after the addition of certain additives to the lubricating oil. Experiments carried out with a medicinal mineral oil suspension of glyceryl monostearate were particularly enlightening. When this suspension is added to lubricating oil in relatively large amounts (above 1 percent), the foam produced may last as long as 5 or 6 hours. On several such occasions, it has been observed that at the end of about 3 hours, nearly the entire foam structure is white. This seems to indicate that the colored lubricating oil has drained from between the layers of glyceryl monostearate (vide infra).

Other additives which have exhibited "thick film" phenomena are Tergitol 08, Penatrol 60, and Span 40. Tergitol 08, in concentrations above 0.1 percent is very effective in preventing the formation of large volumes of foam. However, there remains a stable, residual foam which may be more aptly described as a dense suspension of relatively large bubbles in oil. Typical "macroscopic" films are obtained with dehydrated Penatrol 60 in oil. Such a film, stretched circularly across the cross section of the cylinder, possesses a remarkable elasticity. By admitting air below the surface of the film, it can be extended (convex upward) and blown from near the bottom to the very top of the cylinder without rupturing. Similar films were formed with low concentrations of span 40, though these were not quite as stable. At the glass-oil interface, these films were nearly 1-millimeter thick, and yet they did not apparently drain. They were translucent and, in addition, large particles (presumably of the additive) could be seen supported in and on the stable film. These afford good examples of inhomogeneous films which are nevertheless particularly stable. Another interesting phenomenon concerns the way in which these films rupture. They do not burst suddenly as most films do, but rather, they tear very slowly. A hole is formed, generally near the center of the film and then slowly spreads outward; the complete destruction may take as long as 2 or 3 seconds.

Much of the foregoing description, though it consists chiefly of empirical observations, may contribute substan-

tially to the theoretical considerations involved in the formation of stable oil foams. On reviewing these observations, it may be realized that a definite parallelism exists between the theoretical "plastic films" described by Wilson and Ries (reference 9) for aqueous systems and those described here. These films

- (1) Were of microscopic thickness and showed no signs of draining
- (2) Remained immobile over a period of several hours
- (3) Showed definite evidence of structure (as with the glyceryl monostearate films)
- (4) Could be stretched considerably without rupturing
- (5) Supported solid, immobile particles in their surfaces
- (6) In breaking, did not burst, but rather tore slowly

The "plastic film" concept of Wilson and Ries is based on the experimental observation that the surface viscosity of aqueous solutions giving stable films is substantially greater than the bulk viscosity of those same solutions. The picture presented by these authors consists of a liquid, mobile layer sandwiched by two solid films of finite thickness. These thicknesses, as measured in their experiments, varied from 0.001 to 0.004 centimeter. Such considerations may readily be applied to the systems containing lubricating oil plus the various additives mentioned. In this instance, the oil would be held between the two layers of the oriented additive. The oil films, however, are considerably thicker because of the higher viscosity, and the higher concentration of additive, and their greater tendency to orientation. Thus here there may be a thick plastic film adsorbed upon the surface in addition to semi-immobilized layers of oil beneath it.

It is noteworthy that those additives which give thick films under certain conditions are very excellent antifoaming and defoaming agents under other conditions. The conditions concerned are concentration and the presence or absence of small amounts of water. Span 40, for example, at concentrations of 0.01 and 0.5 percent, is an excellent foam stabilizer. At a concentration of 0.1 percent, this same additive is a very effective foam breaker and antifoam. Similarly, Penatrol 60, in the absence of water is a stabilizer; in its presence,

the foam is decidedly unstable. These results tend to substantiate the view that oriented films of additives (or of other foreign constituents) are responsible for foams of extreme stability.

Foams of High Density

Foam densities are determined by simply dividing the weight of liquid in the foam by the total volume of foam.

In the experiments with lubricating oil, two types of high density foam have been observed, the one being very stable and the other extremely unstable. The very stable foams having thick films have been described in the previous section. In this case the oil is contained within the films. Only rarely do the densities of such foams exceed 30 percent. On the other hand, unstable foams of high density are relatively common. In this case, the liquid is dispersed irregularly between bubbles of gas, the bubbles bursting or coalescing faster than the liquid can drain. These are examples of foams described in the section on units of measurement in which L_l , the average life of the liquid in the foam, is greater than L_g , the average life of the gas in the foam. These experiments serve to illustrate the fact already pointed out that drainage is not essential for film rupture.

High density foams are nearly always observed when very effective antifoaming agents are added to lubricating oils at room temperature. In fact it may be said that such packing is invariably obtained when the additive prevents the formation of a large volume of foam. However, the converse is not necessarily true; that is, high density foams are not always unstable.

For example, foam densities of 55 to 60 percent have been observed with lubricating oil (Aeroshell 120) containing 0.1 percent Alronol. This value is more than twice as high as the theoretical void space of 26 percent for uniform spheres. For the explanation of this phenomenon, it is necessary to look to abnormally slow drainage of the viscous oil rather than to the structure of the outermost surface.

Theories of Antifoaming

Introduction.— In the study of foaming in aviation oils, the experimental work soon revealed two types of action of

of chemical agents added to inhibit foaming. Some have a "defoaming" action, so that a foam once made, for example, by a gas bubbling method, collapsed with much greater rapidity than did a foam of the original oil. Others had an "antifoaming" action, preventing the formation of a foam at all, using a bubbling method. In the latter case, air introduced by beating or stirring also separates as soon as it can reach a surface from which to escape. The two terms will not be distinguished in the discussion to follow. However, the residual foam that accumulates in spite of the presence of certain antifoamers may be very stable, showing a defect in defoaming action. It may be significant to note that antifoamers are rare, and those found are effective only in limited applications, although defoamers for various conditions are common.

Except for Foulk's theory, the principal considerations applied to the theories of foam inhibition outlined below are specific molecular interactions between the foaming and defoaming agents, and physical conditions producing inhomogeneity in the film. A combination of these is suggested and described in detail.

Corollary of the balanced layer theory applied to defoaming (Foulk, reference 19).— "In the case of (aqueous) solutions containing both positively and negatively adsorbed substances, there should be certain mixtures which do not foam because positive and negative adsorption cancel each other and thus produce equality of concentration between surface layer and mass. The same idea can be expressed by saying that the foaming of solutions of positively adsorbed substances will be stopped by the addition of the right amount of a negatively adsorbed material, and vice versa." (Foulk and Miller, reference 3.)

Hazelhurst and Neville were the first to point out the untenable nature of the above corollary, in a criticism (reference 1) the validity of which was acknowledged by Foulk. Obviously, the composition of the surface would not equal that of the bulk liquid merely because the total concentrations in each happened to be the same. That is to say, of the two solutes, one would be present in greater concentration in the surface than in the bulk, while the other would be present in lower concentration in the surface than in the bulk. If each solute alone tended to produce foam by its (positive or negative) adsorption in the surface, the presence of both of them would increase the tendency. This theory is mentioned to forestall its reappearance.

Theories of molecular interaction between foamer and antifoamer.— In supposing that foaming is due to the presence of a foaming agent in the liquid, and further that the foaming agent is effective by virtue of its adsorption at the air-liquid interface, there are several logical possibilities by which an antifoaming agent may interact with a foamer to destroy its foaming ability. The interaction is generally supposed to involve secondary valence forces — for example, of the hydrogen bridge type. Chemical reaction of primary valence bonds is not ruled out by any means, but would be expected only infrequently.

1. Antifoamer and foamer may mutually exclude each other from the surface.
2. The antifoamer and the foamer mutually coagulate and are thereby removed from the surface.
3. The antifoamer is sorbed on the foamer, or vice versa, and the resulting complex is a poor foamer. "Sorbed" is used here rather than "reacts" to avoid the necessary implication of stoichiometric proportions. However, either definite association compounds or micellar sorption complexes of continuously varying composition must be considered. The former may account for the behavior of substances which are defoamers at low concentration and become foam stabilizers above a certain concentration. The latter seem more likely to account for the behavior of substances which give both maxima and minima in their defoaming action as the concentration is varied, possibly corresponding to changes in the dispersion of one or the other of the agents and the formation of micelles.
4. The antifoamer excludes the foamer from the surface and is itself a poor foamer. (This idea considers the air-liquid interface as a surface analogous to solid surfaces; on which preferential adsorption takes place, a less strongly adsorbed substance being rapidly displaced by a more strongly adsorbed substance. It is by no means possible to enumerate the properties a substance must have to cause it to be adsorbed strongly at the air-liquid surface, but not to stabilize a foam. Talmud (reference 10) suggests something of the same sort in his theory of hydration of monomolecular films; namely, that a strongly adsorbed film not greatly hydrated does not form very stable films.)

5. The antifoamer and the foamer both collect in the surface and oppose each other in some unspecified way. This requires highly specific properties of the antifoamer in relation to the foamer and the solvent. If the surface is a gel stabilized by the foamer, an antifoamer which would cause the gel to become liquid may be pictured, acting in a manner similar to certain salts upon aqueous gels.

Defoaming Caused by Inhomogeneity of the Film

1. Hughes' theory (reference 21).— A definite tendency for antifoaming agents to be only slightly soluble in the solvent of the system has suggested that their action was due to small droplets in the film, which so weakened it as to form a point of rupture. Hughes pictures such an insoluble droplet in the liquid forming a film between two air interfaces. As the liquid drains, the thickness of the film becomes equal to the diameter of the droplet. At this point, or shortly thereafter, according to the theory, the droplet becomes a nonuniform region extending clear through the film, analogous to an actual hole, and thus causes rupture. The diameter of the droplet is supposedly large as compared with the thickness of the most stable liquid film; so the droplet cannot be occluded within a stable film.

The theory has a plausible element, but is not elaborated by Hughes. In order to stay immersed in the liquid of the film, the droplet must have the properties necessary to form a stable emulsion within the liquid. That is, it must in itself have sufficient adhesion with the surrounding liquid to resist the cohesive forces of the liquid which would otherwise eject it from the film and cause it to "float" upon the air-liquid interface, where, as an immiscible, nonspreading droplet it would remain inert. If, however, the droplet does exist as a stable emulsion within the liquid, the forces holding it there, so that it is not ejected at a film surface, must be at least equal to the cohesive forces within the liquid itself. Hence, the interfaces between the liquid and the droplet can scarcely be a point of fracture any more than any other cross section of the film, and a small spherical liquid drop possesses great strength against being pulled asunder.

If the adsorbed layer of stabilizing agent, which must be on the air interface of the film, is taken into account,

the theory is more plausible. Although the droplet is wetted by the liquid, it does not necessarily follow that the stabilizing agent will form a layer over the droplet, when the film thins to the point where such a film must form or the layer of stabilizing agent be perforated. For lack of information, the possibility must be admitted that, by such a perforation of the stabilizing layer, an immiscible droplet in a stable emulsion in the system could cause rupture of the films and hence act as a defoamer.

Instances have been observed in carrying out the pop test where the opposite is true; the agent, added from a platinum wire to a thin film of oil in a loop of platinum wire, will be wetted by the oil, but will form a lens extending through the film. Due to the color of the oil, it was easy to see the "windows" formed by droplets of the agent in the stable film, which still remained stable. Of course it was impossible to see whether there was an oil film over the lens.

2. Inhomogeneity caused by volatility.— Evaporation of either solvent or solute causes differences in concentration at the surface which must be equalized by diffusion or convection of the liquid in the film. It is obvious that loss of a stabilizing solute must decrease the foaming ability. Evaporation also causes temperature differences, the thin portions being cooler because of their smaller heat capacity (reference 8). However, Neville and Hazelhurst show that evaporation may actually stabilize films of presumably pure liquids held on small wire loops. Talmud, too, observed that evaporation of solvent stabilized the film; whereas evaporation of solute decreased the stability.

With aeronautical oils, volatility is a significant property only in connection with the retention of the defoaming agent at elevated temperatures. No volatile constituents affecting foaming appear to be in the original oils.

3. Inhomogeneity caused by concentration differences.— More important to defoaming are the concentration differences caused by contact of the foam with another liquid, or its vapor, not already disseminated through the system. Ether vapor, for example, is very effective in breaking aqueous soap foams, although stable foams may be made with the solution previously saturated with ether, or blown with air containing ether vapor. The effect is evidently due to strains

set up by the local differences in concentration either between different areas on the film or between the inner and outer layers.

A similar effect is noted in many cases in the pop test (appendixes II and VI). The data on the pop test show that good defoamers have always given positive pop tests, but many substances that are not good defoamers likewise give a positive test. In some of these, great storms and vortices can be seen in the film, shooting out from the point of contact of the agent with the oil film, before the film bursts. When these same substances are then homogeneously dispersed in the oil, the mixture will foam as well as or better than the original oil. It must be noted that differences in concentration, per se, do not necessarily produce rupture. Many of the agents giving a negative pop test are soluble in the oil and spread through it without causing the film to break. Therefore, rupture of the film is caused in these cases only by certain agents and only when nonuniformly dispersed,

4. Inhomogeneity caused by physical shocks.— Sudden expansion or contraction of films (e.g., soap films on a bubble pipe, or more especially, foam on lubricating oil) will frequently cause rupture, while slow expansion or contraction may be carried out to produce multifold changes in size. It would seem that a certain time of adjustment is necessary to equalize the strain or rearrangement or redistribution of material produced in the film.

A hot wire (say 50° C hotter than the film) will always rupture a film touched by it, even though the film is large and the wire small. An even more striking example is afforded by a column of foam of aviation oil in a glass tube surrounded by an electric wire heating element. With temperature equilibrium established, a long column of stable foam was formed by very slow bubbling of air. The input of electricity to the heater was increased slightly, setting up a new temperature equilibrium in several minutes, 2 or 3 degrees higher than the first. The foam column, however, responded to the increased heat immediately by beginning to break, and in about 1 minute, the entire column collapsed. In several minutes more, a new column at the slightly elevated temperature had formed, apparently as stable as the first. This is further evidence of extreme sensitivity to temperature gradients. These facts may be interpreted as indicating an easily reversible surface structure, perhaps

something like a gel, which becomes liquid when disturbed but quickly becomes solid again when quiet. Following the same theme, mechanical working may prevent the formation of the surface structure so that its detection would be elusive when measured by a surface viscosimeter in the usual ranges.

Combined theory, applied to aviation oils.— The following suggestion (Robinson) of defoaming and antifoaming mechanism has been developed principally from experience with the pop test.

The antifoamer is considered to be essentially molecularly dispersed in the foaming system, or at least to be in a sufficiently finely divided state that it has free mobility through the liquid. When an air interface forms, as a film is made, the foaming "agent" is adsorbed and a definite layer with structure is set up on the surface. This layer of foaming agent provides a surface such that the antifoamer, which in all known cases in the oil systems studied is a polar — nonpolar compound, adsorbs and orients with the hydrocarbon part of the molecule linked with the structure on the surface, leaving the polar part of the molecule directed inward within the liquid in the center of the film. This polar surface so powerfully repels the oil that it withdraws into itself from between the two air interfaces. There would then be left a film a few molecules thick, comprising the two outermost "skins" of the film, and containing both the adsorbed foamer and antifoamer. Presumably, the structure would be disturbed so greatly by the inward-turned polar groups, that rupture would occur considerably before extreme thinning took place. On the basis of the explosive rupture of films observed in the pop test, it seems even more likely that the polar groups of the antifoamer immediately destroy the deep surface structure that made the film stable, and the hydrocarbon draws up into drops and the film explodes. In the case of a very powerful antifoam, the action would be expected to be so rapid that a liquid film would be too short-lived for a real foam to form at all.

However, it must be remembered that a pop test involves approaching the film from one side only.

In support of this suggestion, certain experimental evidence in connection with the pop test and its antecedents is pertinent. After placing a drop or crystal of substances

that were defoamers for aviation oil on a thin film of the oil on a glass plate, the oil film withdrew completely after several minutes from the drop or crystal, leaving a circular patch of bare glass. Nothing visible could be scraped off the surface of the glass; so the film left must have been very thin. Droplets of oil would not wet the surface of this patch, while water spread instantly. Furthermore, the test was extended to brass surfaces, which are preferentially wetted by oil, with the same effect, and this observation led to the supposition that the action was independent of the type of surface and should work at an air-liquid interface. The final result was the development of the pop test (appendixes II and VI) which is known to be significant for several foaming systems other than aviation oil (appendix VI). The spreading tests on the solid surfaces showed that the defoaming agent oriented to form a water-wetting and oil-repelling surface. However, since the glass was already oil wet, and the brass is preferentially oil wetting, it was concluded that the agent must not orient directly on the solid surface, but rather on an oily film which was already formed on the solid surface. This explanation accounts for the fact that the test is independent of the nature of the surface, and is consistent with a single layer of defoamer oriented so as to present its polar groups inward toward the oil film.

Summary

1. The theories of foam developed for aqueous systems by Plateau, Wilson and Ries, Foulk, and Talmud, postulate positive adsorption of a foaming agent in or upon the surface, producing a plastic coating (Plateau, Wilson and Ries), or a solvated monolayer (Talmud), or a mere difference in concentration (Foulk) which requires work to undo in destroying the film. The latter conception here is generalized by extending it to any spontaneously arising difference between surface zone and bulk liquid, including the segregated electrical charges always occurring at surfaces. This is further developed to embrace the suggestion (Hardy, McBain) that the surface causes orientation of chains of oriented molecules extending from it into the neighboring liquid, partially immobilizing it, and in extreme instances bridging across the oil bubble film from inner to outer surface. Further evidence is drawn from observed cases of thick oil foam films and their rates of drainage.

2. The theories of antifoaming action and of foam breaking are similarly reviewed and developed in view of the general theory of foam here developed for oil foam. It is shown that inhomogeneity of a film frequently causes it to rupture, although in other cases such a film is stable or even of enhanced stability. When the former mechanism is operative, it is one of the most effective means of breaking foam. Since foam is always a result of adsorption or rearrangement of the surface of an otherwise nonfoaming liquid, suggestions are developed as to how an antifoaming agent can upset this arrangement or distribution.

APPENDIX II

METHODS OF MEASURING FOAM

A review of foam-measuring methods (reference 22) led to a classification based on the relative importance of (a) drainage, or (b) film rupture, as operative factors in the collapse of the foam. The foaming of lubricating oils cannot readily be studied at room temperature by methods of the former class, because the viscosity of the liquid makes drainage a very slow process. At higher temperatures, where the viscosity is considerably less, methods of both types are applicable. When compared with other foam-forming systems, such as those of appendix VI, lubricating oil cannot be considered as having a great foam-forming capacity. As a result, the greatest problem in all methods of foam measurement with aeronautical oils is to get an adequate volume of foam for the purpose. The three chief methods customarily employed are listed immediately below. They are followed by a description of the techniques employed using each of the three methods. The code classification of techniques is based on the three methods and is consistent throughout the report.

Methods of Producing Foam from Lubricating Oils

1. Mechanical shaking or beating.— At room temperature the viscosity of lubricating oil is too great to permit the production of a foam merely by shaking by hand. More vigorous mechanical shaking or beating produces a fine "emulsion" of air in the oil. The quantity of air dispersed may equal the volume of oil and the degree of dispersion may be very fine. The life of this foam is of the order of 60 minutes at room temperature for undoped oils.

At 100° C production of foam by mechanical shaking or beating is more successful. The stability and the volume of the foam are greatly reduced. The order of magnitude of the foam stability is 1 to 2 minutes, starting with 180 cubic centimeters of lubricating oil.

2. Evacuation.— Reduction of the air pressure above a sample of oil results in the production of a large volume of foam. Assume the validity of Henry's law for the solubility of air in oil and information concerning the solubility already published (references 23, 24, and 25); then at all pressures the solu-

bility of air in oil is of the order of magnitude of one-tenth by volume. Suppose an average temperature for the oil in aircraft lubricating systems to be 180° F; then the following table gives the volumes of air released per unit volume of oil at different altitudes. In terms of foam this takes into account only the presence of dissolved air and not the operation of other foam-forming causes, such as mechanical agitation, or the expansion of finely suspended air as described. For an estimate of foam volumes in actual operating conditions the values in column 3 would be approximately tripled, first because of the presence of dissolved water which has approximately the same solubility as air in oil, then also because of the presence of other volatile liquids, such as gasoline, which correspondingly increase the volume of froth to be expected.

TABLE I.- ESTIMATED AMOUNTS OF FROTH FROM
LUBRICATING OIL AT DIFFERENT ALTITUDES

Altitude in feet	Pressure in atmospheres	Volume of air released from unit volume of oil at 180° F
0	1	0
20,000	.44	.12
25,000	.38	.17
30,000	.30	.24
35,000	.23	.32
40,000	.18	.46

Methods of foam measurement employing evacuation are more useful at room temperature. The time taken for the complete collapse of a foam formed from 100 cubic centimeters of oil at a pressure of 5 millimeters is of the order of 40 minutes. At 100° C this time is only 1 or 2 minutes. In order to produce greater volumes of foam, beating or aeration is frequently used before the evacuation procedure.

3. Bubbling.— Although the process of bubbling a gas through the oil has no exact counterpart under actual operating conditions it has already found favor in a number of previously published foam-measuring methods involving other liquids. Its disadvantage lies in the possibility that the stability of a foam produced in this manner may not correspond to results obtained in practical flight tests. However, the present results, so far as they have been carried, do not indicate any disagreement between beating and bubbling procedures. The very great advantage of bubbling is that it readily provides an adequate volume of foam on which measurements can be made, even at higher temperatures where the other methods of foam production are less effective.

Technique of Foam Measuring Methods

1a. Easy Mix Blender.— The stirring device described by this name was used only in the early work on foam-measuring methods. The technique of using it has not been developed into a method that will give reproducible results.

1b. High temperature beating test.— It is necessary in this test to be able to see the volume of foam produced and follow its rate of collapse. A glass-jacketed Pyrex beaker is therefore employed; the outer jacket contains the liquid having a boiling point suitable for the temperature range to be investigated. A sturdy metal paddle or propeller is introduced into the inner beaker through a small opening. The inner beaker is kept covered as much as possible to keep down losses of oil by splashing and to prevent condensation of the heating vapors in the sample. The following dimensions and quantities have been found suitable.

Volume of inner beaker, cc	600
Volume of oil sample, cc	180
Time to reach thermal equilibrium, min.	15
Time of stirring, sec	30

After the foam has been produced by whipping for 30 seconds, the time is measured to the first appearance of the oil surface through the foam. The results have a reproducibility of ± 3 percent. The order of magnitude for lubricating oils is 60 seconds at 100° C.

1c. The Towne Foam Test.— Two hundred grams of the test oil are weighed into an 800-milliliter beaker and heated to 175° F and maintained at this temperature for 30 minutes. It is then allowed to cool to room temperature by standing overnight or for a sufficient period so that room temperature is attained. No artificial means of cooling is permitted.

The oil is then stirred at the top speed of a Sunbeam Mixmaster for exactly 3 minutes; the stirrer paddles are allowed to drain for 15 seconds, and then the entire contents of the beaker are poured quickly into a 500-milliliter graduated cylinder. The pouring and draining period is not continued beyond 1 minute after the stirrer is stopped. In the original specifications the volume of foam is read at 0, 10, 20, 30, 40, 50, and 60 minutes, starting with zero time 4 minutes after the stirring operation is begun; in this laboratory, readings are continued at suitable intervals until complete collapse of the foam.

The revolving plate with which the Sunbeam machine is supplied and which is intended as a holder for bowls is removed from the machine for this test. The beaker of oil rests directly upon the base plate when the oil is being stirred and it may be necessary to hold it by hand so that the stirring mechanism does not come in contact with the walls of the beaker during the stirring period.

The test is performed at room temperature and where close comparisons are to be made a reference oil should be run at the same time or within a few hours to insure duplication of atmospheric conditions.

1d. Test-tube-shaking method.— A simple method of testing the foaminess of liquids of low viscosity is to shake a test tube containing the liquid and observe whether or not foam can be formed in this way. The production of a stable or unstable foam also can be observed. The method has been used by Wilson and Ries (reference 9) in their comparative studies of foaminess and surface viscosity.

2a. Beating and evacuation.— Even at room temperature it is frequently desirable to ensure the production of a greater volume of foam than can be obtained by evacuation only. This is achieved by a preliminary beating or aeration for a specified length of time. It has been found that the preliminary treatment must be of exactly the same type, and

last for the same period of time, when several samples are to be compared, because otherwise results are not reproducible. A suitable apparatus for preliminary beating is a thin glass propeller which can be connected to an electric motor and inserted in the neck of the 200-cubic centimeter flask used in the evacuation technique. After 60 seconds of stirring the rest of the technique is the same as in method 2c.

By immersing the flask in boiling water, a test may be made at 100° C which gives very approximate results.

2b. Aeration and evacuation.— When aeration is employed as a preliminary measure before evacuation, a suitable apparatus consists of a drying tower filled with calcium chloride and a 300-cubic centimeters gas wash bottle, both of which are connected in series with a Hyvac pump. With the pump in operation, air is drawn through the drying tower and allowed to bubble continuously through 75 cubic centimeters of the sample. This aeration is continued for a period of three minutes. At the end of that time the stopcock between the tower and the bubbler is closed and the immediate reduction in pressure in the bubbler produces a large volume of foam. When the vessel is completely filled with foam, the connection to the pump is closed and the subsidence of the foam height is measured every minute until the surface of the oil just becomes visible through the foam. The order of magnitude of the result is 15 minutes and the deviation ± 3 percent.

Using the same apparatus as that just described, method 2b can be applied to tests at 100° C by immersing the gas wash bottle in boiling water. Presumably it also can be successfully applied at temperatures between 20° and 100° C. The results at 100° C are clearly defined and reproducible. The method offers the further advantage of being extremely rapid. After setting up the apparatus, the entire test can be carried out in a few minutes.

2c. Evacuation at room temperature.— Production of foam by evacuation alone, without any preliminary attempt to incorporate air in the oil, is useful only at room temperature; at higher temperatures the relative instability of the foam coupled with the small amount obtained by this technique makes the final time-reading of a low order of magnitude, resulting in a high percentage deviation.

A 200-cubic centimeter round-bottomed flask, containing 20 cubic centimeters of the oil, is connected to a Hyvac pump and a manometer. Evacuation of the system results in a volume of foam that fills the container. The time for this volume of foam to collapse to within 1-centimeter height of the oil surface is measured, the system being maintained at reduced pressure.

3a, 3b. Bubbling method at different temperatures (fig. 1).— For observing the foam behavior of oils at different temperatures, the foam meter is jacketed. Liquids of suitable boiling points are heated to obtain constant temperature and their vapors are condensed and refluxed. The following liquids provide a temperature range from 46° to 100° C.

<u>Liquid</u>	<u>Boiling point</u> (deg C)
Carbon disulphide	46
Acetone	56
Methyl alcohol	64.5
95 percent ethyl alcohol	78
Water	100
n-butyl alcohol	117

About 20 cubic centimeters of sample is used. Nitrogen gas previously dried over calcium chloride and flowing at constant pressure, is introduced through a porous bubbler (method 3a) or through a sintered glass membrane (method 3b). The top of the foam meter is connected to an apparatus designed to measure the volume of gas displaced by the foam, thus providing information on the rate of gas input. Before any readings are made, an initial foaming of the sample is performed to make it homogeneous and to aid in the dispersion of any additive that may be present. Furthermore, the first foam is often more stable. This foam is allowed to collapse completely before the determination is started. After foaming for 10 minutes, the levels of both the liquid and the foam are repeatedly observed until total collapse of the foam. The data obtained are used to obtain the variation

with time of the amounts both of gas and of liquid in the foam. Methods 3a and 3b differ in the type of bubbler used and also in the diameter of the foam column, so that while the results are comparable they are of different numerical magnitude.

3d. Beaker bubbler method.— Substances which appear of outstanding interest as defoamers are tested over a range of temperature by a simple bubbling method. A sintered glass bubbler on a glass tube connected to a low pressure air or nitrogen supply is kept immersed below the surface of the liquid to be tested, in a small beaker. The bubbling goes on continuously while the beaker is slowly heated over an open flame and the foam, if any, noted over a range of temperature. With a perfect defoaming agent, every bubble breaks the moment it reaches the surface, while less effective agents permit the formation of a small head of foam. This simplified apparatus is not suitable for the quantitative measure of foaming, but permits immediate recognition of a nonfoaming liquid. The study of the temperature effect is of great interest, as the foaming characteristics of liquids frequently change greatly with temperature, and furthermore, defoaming agents may be irreversibly changed in regard to their defoaming action upon passing through a temperature cycle.

This method is used extensively in the evaluation of agents. (See appendixes IV and V.)

3e. Bubbling method at room temperature.— It already has been pointed out that at room temperature it is more suitable to employ methods of foam measurement emphasizing film rupture, because of the great viscosity of the lubricating oils to be investigated. The method of Bikerman (reference 26) was first adopted, although several modifications were introduced. The shortcomings of the Bikerman method have been discussed (reference 22), even though a number of the criticisms had been anticipated in a paper by Hoffmann and Peter (reference 27), not available in this country until recently. The method used at Stanford University was found to be identical with that recommended by Hoffmann and Peter.

A single capillary is used to form the foam, which is thus comprised of bubbles of identical size. The rate of gas input was measured by the rate of displacement of the air above the liquid, although it could have been obtained from

the rate of rise of the foam volume, as was done by Hoffmann and Peter. When equilibrium was attained, there was no further rise in the foam height. It was observed that the bubbles broke only at the top of the foam and that no coalescence took place in the bulk of the foam. These conditions do not hold for many aqueous systems, but they are a sine qua non of the Bikerman unit of foaminess, the "average lifetime of a bubble" in the foam. The quantities measured are the average maximum foam volume v and the volume of gas V passed through the capillary in the time t . The average lifetime of gas in the foam, designated L_g is then given by the expression

$$L_g = vt/V \quad (1)$$

This unit is mathematically identical with the sigma of Bikerman and the tau of Hoffmann and Peter, although it is capable of a wider application because less restricted by assumption and interpretation. The theory of those units is discussed in reference 22.

Units of Foam Measurement

1. Derivation of Units.— The average length of time that unit volume of gas remains in the foam has been mentioned previously as a unit of foam measurement (L_g). More direct perhaps is the use of the average lifetime or unit volume of foam L_f defined as:

$$L_f = \frac{1}{f_0} \int_0^{f_0} t \, df \quad (2)$$

where

f_0 volume of foam initially

f volume of foam at time t

If l and g denote the corresponding volumes of liquid and gas in the foam, then:

$$L_f = \frac{1}{l_0 + g_0} \int_0^{l_0} t \, dl + \frac{1}{l_0 + g_0} \int_0^{g_0} t \, dg \quad (3)$$

since

$$f = l + g \quad (4)$$

The value of L_f is in providing a single number to express foam stability. Using the same foam meter and taking care to produce foams always under the same experimental conditions, then values of L_f can be used to compare the relative foam stabilities of several samples.

The unit L_f can itself be divided into two component parts - the average lengths of time that unit volumes of gas (L_g) and liquid (L_l) remain in the foam. Those units have already been defined (reference 28) as

$$L_g = \frac{1}{g_0} \int_0^{g_0} t \, dg \quad (5)$$

$$L_l = \frac{1}{l_0} \int_0^{l_0} t \, dl \quad (6)$$

The relation between L_f , L_g , and L_l depends on the initial relative foam density d_0 defined as

$$d_0 = \frac{l_0}{g_0 + l_0} \quad (7)$$

In practice it is more practicable to obtain values of L_l , L_g , and d_0 and then calculate L_f from the equation:

$$L_f = L_g + d_0 (L_l - L_g) \quad (8)$$

Equation 8 is readily derived from equations (2) and (4).

Values of L_l and L_g are useful in the analysis of the factors that have affected the stability of the foam. A discussion of the stability of foam and its measurement (reference 22) used the concurrent phenomena of

drainage and film rupture as a basis for the differentiation of foam-measuring methods. The use of the preceding units makes clear the part played by each of those phenomena in the case of any given foam. If drainage is a more pronounced factor than film rupture, as is normally the case, especially when the foam is freshly formed, then liquid is removed from the foam at a faster rate than gas is liberated. Consequently L_g will be greater than L_l . If, on the other hand, film rupture or coalescence of bubbles takes place before drainage has had time to assert itself, then the gas is liberated from the foam before the liquid. This happens more frequently in the presence of an antifoaming agent, capable of destroying relatively thick films before they have time to drain. Here L_g is smaller than L_l . It is consequently extremely informative in the case of any single foam to have values of both L_l and L_g .

The advantage of those units is illustrated in the correlation that exists between the dynamic foam meter (No. 3e) and the static foam meter (No. 3a). Previous attempts to correlate dynamic and static methods have failed (reference 29) because the units in each case were not strictly comparable. In fact, it is now clear in the light of the present analysis (by A. P. Brady) that in the previous work L_l was compared to L_g , with which it does not necessarily bear any correspondence. Table II compares values of L_g measured dynamically and statically and shows that the same ratio can be obtained for different samples of oil. Further examples are given in appendix III.

TABLE II.— COMPARISON OF RESULTS OBTAINED BY
DYNAMIC AND STATIC METHODS

Sample of oil	Method of measurement	Formula for L_g	Value of L_g at 25° C (min)
Squibb mineral	Dynamic No. 3e	$L_g = vt/V$	11
Aeroshell 120	Dynamic No. 3e	$L_g = vt/V$	55
Squibb mineral	Static No. 3a	$L_g = 1/\epsilon_0 \int_0^{\epsilon_0} t \, d\epsilon$	7.1
Aeroshell 120	Static No. 3a	$L_g = 1/\epsilon_0 \int_0^{\epsilon_0} t \, d\epsilon$	32.0

Values of L_g and L_l are not independent of the apparatus or of the volume of sample used, but those variables merely introduce a constant factor which does not affect either the ratio of L_l to L_g or the comparison of results for a series of samples. (See appendix III.)

2. Calculation from data.— In every case where values of L_f , L_g , and L_l are desired, it is necessary to observe the variation with time of two interfaces, the foam-liquid interface and the foam-gas interface. To obtain L_g , the volume of gas in the foam at appropriate intervals is plotted against the time, and the area under the resulting curve obtained by one of the several standard graphical methods. To obtain L_l , the same procedure is followed, using the volume of liquid in the foam on the volume axis. By this method it is not necessary to know the mathematical equation that expresses either drainage or rupture of the films, as the integration is performed graphically. In some cases, however, it is observed that a linear or an exponential relation holds and the integration can be readily performed mathematically without the necessity of taking many data or plotting the experimental points. Both graphical and mathematical integrations are used in the course of the present investigation (cf. appendix III.)

Rapid Methods for Testing Foam Inhibition

1. The pop test.— The apparatus for the pop test is shown in figure 2. A ring (7 mm diam.) is at one end of a short length of platinum wire, the other end of which is sealed to a glass handle passing through an oversize hole in the large stopper closing the 250-milliliter beaker. The ring is always flamed before use. A small open hole in the side of the beaker near the bottom permits the introduction of a second platinum wire, which has been flamed and dipped in the reagent to be tested. A small beaker (10 ml) inside the large one serves as a ready supply of the film-forming liquid, near the proper temperature. The ring is dipped into the oil and withdrawn to form a film. The second platinum wire, wet with the reagent to be tested, is introduced, held for a moment to reach the temperature of the air inside, and touched to the liquid film on the platinum ring. A positive test is rupture of the large film, immediately or in a few seconds; otherwise the film remains intact.

The pop test has been applied to several foaming systems other than those herein mentioned, with results given in appendix VI.

Since comparatively few foaming tests have been made at 100° C, a list was made up of substances giving a positive pop test, most of which then were tried by foaming tests. Only a few of the substances giving negative pop tests have been tested by foaming tests at 100° C.

Statistics on the pop test results for aviation oil (Aeroshell 120) defoamers are tabulated below:

Total number of substances tested by the pop test . . .	225
Number giving a positive test	37
Number giving a delayed or indecisive test	17
Number giving a negative test	171

The delayed or indecisive tests are regarded as positive in the figures below:

Number of substances giving a positive pop test tested by foaming methods at 100° C = 38

Number rated by foaming method as:

No effect	25	(66 percent)
Slight defoamer	11	(29 percent)
Defoamer	2	(5 percent)

Number of substances giving a negative pop test tested by foaming methods at 100° C = 16

Number rated by foaming method as:

No effect	11	(69 percent)
Slight defoamer	5	(31 percent)
Defoamer	0	(0 percent)

From this and similar tables, the following generalizations have been made:

1. A negative pop test indicates that an agent is not a strong defoamer, although it may have a slight defoaming action.
2. A good defoamer always will give a positive pop test.
3. An agent without effect on the foaming ability, or a slight defoamer, may give either a positive or a negative pop test.

However, in a few of the cases where positive pop tests were given by substances reported to have no defoaming action in direct foam tests, the concentration of the agent was shown to be responsible for the discrepancy. Only some of the cases from which the above figures were collected have been tested thoroughly over a concentration range. It has been demonstrated repeatedly that agents may act either as foamers or defoamers in the same system, dependent only upon concentration.

The advantages of the pop test are its speed and small consumption of material. Seventy agents have been tested in 1 day, observing proper care and repeating each test at least once, and checking doubtful cases many times. Only a few milliliters of the foaming liquid are required, and enough of each defoaming agent to wet the tip of a platinum wire.

2. The ring test.— The apparatus consists of a series of circular rings of platinum wire, with attached glass handles, and a porcelain test block. Rings of 1-, 2-, 3-, 4-, 5-, 6-, and 7-millimeter diameter have been found to cover a range suitable for this work. The test consists in picking up a film of liquid on a ring and holding the ring with its plane vertical and its lower edge touching the liquid surface. In this way, the shape and the size of the film is defined, and at the same time drainage takes place freely. The persistence of the film is timed with a stop watch from the moment the ring is drawn up through the liquid surface, although occasionally it has been convenient to determine the largest diameter of film which would persist for a given time, say 10 seconds.

A similar and more highly refined method to obtain percent film formation has been published by Foulk and Barkley (reference 30) since this report was first submitted.

As an example of a determination of the effect of concentration on film-forming ability, the film persistence of a series of solutions of Span 20 (commercial sorbitan monolaurate, Atlas Powder Co.) in a clear white mineral oil of low viscosity is cited in table III. This substance has been reported as both a foamer and a defoamer, and the concentration study clearly resolves the anomaly.

TABLE III. - RING TESTS OF SPAN 20 IN WHITE
MINERAL OIL AT ROOM TEMPERATURE

Concentration (percent)	Persistence when	
	Quiet	Stirred
4.96	17 min	17 min
1.31	17 min	17 min
.12	17 sec	3 sec
.012	2 sec	1 sec
.0013	15 sec	4 sec
Oil alone	47 sec	

The necessity for two columns, "persistence when quiet" and "persistence when stirred," illustrates an intrinsic difficulty in correlating the single film method with direct foam methods. In the latter, the production of the foam automatically provides more or less stirring, and adsorption occurring at a quiet surface is correspondingly prevented. However, in single film studies the concentration of surface active agents in the film depends upon the undisturbed life of the surface; this in turn determines film stability. This effect complicates an empirical expression of results, although it affords grounds for the explanation of some peculiar foam phenomena.

The advantages of this test are in its rapidity and small consumption of material. Solutions were made up in 10 milliliters quantity by weighing on an analytical balance, permitting accuracy and great ease of handling. The method has not been refined as regards shielding from drafts, temperature control, and so forth. In the cases where direct comparison with other foam-testing methods has been possible, qualitative correlation has been found. The method cannot be used to measure quantitatively strongly foaming liquids; the time of persistence is irreproducible past a few minutes, appearing to depend upon accident rather than upon a property of the liquid.

The Single-Bubble Method for the Study of Foaming

In earlier work in this laboratory by Lindquist, bubbles of air were injected with a syringe pipette under the surface of a liquid in a vessel open to the atmosphere (fig. 3). The

life of the bubble was timed from its arrival at the surface until it broke, and the variation of bubble life with bubble volume was obtained. At a certain critical volume bubble life increased sharply, making the curve almost vertical (fig. 4). The critical volumes, for the series of lubricating oils studied, were so far apart that the curves for different oils scarcely overlapped. This phenomenon was so striking that the original work was followed up to refine and extend it.

A precision apparatus for delivering bubbles of known volume was constructed, since a large fluctuation in the lives of different bubbles of the same size in the same oil was ascribed to errors in this measurement. The liquid surface upon which the bubbles float was arranged to be under cover and undisturbed at all times, except when the bubble itself came up. Measurements were made upon four oils and upon some modified samples of them. The apparatus is depicted in figure 5.

The results of these experiments confirmed some of the preceding single bubble work. A similar wide fluctuation in the lives of different bubbles of the same oil was found; it was shown that it could not be due to variations in bubble volume, falling dust, or drafts. In the range of bubble volume studied (the same as in the original work), any effect of bubble size upon bubble life was much smaller than the variation between the lives of different bubbles of the same size. The lives of single bubbles of Aeroshell 120, NACA reference 120, and Texaco 120 oils were in the approximate ratio of 7000:10:1. This does not coincide with the relative magnitude of foam stability found by other methods, but does agree with the curves obtained in the original single bubble work of Lindquist in that for the same size of bubbles, bubble life in the different oils could not be expressed on the same scale.

The use of the single-bubble method to demonstrate a nonfoaming liquid is satisfactory. For example, NACA reference oil, cooled below 0° C for several hours, has been shown not to foam for several hours more after reaching room temperature. After standing at room temperature a day or so, or upon being warmed, the oil regains its original foaming ability (appendix VII). This effect is clearly demonstrated by the single bubble method. The data are summarized in table IV.

Another example of the single-bubble method used to demonstrate a nonfoaming liquid is included in table IV. A series of Span 20 solutions in a clear white mineral oil were tested. Span 20 is a foam stabilizer in high concentration, a defoamer in low concentration, and has little effect in traces. This is shown clearly by the single bubble measurements; there is excellent qualitative agreement between these results and those of the ring test on a quiescent surface (col. 2 in table III).

TABLE IV

Oil	Bubble volume (cc)	Average life (sec)	Number of values	Av. dev. from av.
NACA, chilled	0.106	1.3	20	0.16
NACA, warmed	.106	20.0	11	13.6
Span 20 in mineral oil (percent)				
4.96	.042	300.0	3	148.0
1.31	.042	355.0	3	130.0
.125	.042	3.9	5	3.0
.0117	.042	.5	5	.4
.00127	.042	17.2	4	16.4
None	.042	26.3	9	23.8

Summary

The greatest problem in all methods of foam measurement of lubricating oils is to get an adequate volume of foam for the purpose. Methods of producing foam from lubricating oil are:

1. Mechanical shaking or beating
2. Evacuation after preliminary beating or aeration
3. Introduction of gas through a bubbler

Different techniques of foam measurement that employ these methods are described. The units of foaminess are discussed

and the applicability of the concepts "average lifetime of gas in the foam (L_g)" and "average lifetime of liquid in the foam (L_l)" extended to both static and dynamic foam methods. Methods of calculating the average lifetimes from foam-stability data are described.

Rapid methods for testing foam inhibition are:

1. Film-breaking or pop test
2. Liquid film stability measured by ring test
3. The study of the stability of single bubbles

Data are given, obtained by means of those three methods, and the applications and limitations of each one illustrated and discussed.

APPENDIX III

CHARACTERISTICS OF EXISTING LUBRICATING OILS

Foaming Characteristics

For purposes of comparison, it is necessary to establish the foaming characteristics of existing aeronautical lubricating oils by the various foam tests in current use. The simplest and quickest method of measuring foam is aeration followed by evacuation. This method is especially useful at room temperature, where the viscosity of the oils is such that they may be filled readily with finely dispersed air bubbles, either by beating or by bubbling air through them. The stability and volume of the foam resulting upon evacuation of this mixture depend upon the amount of suspended air; hence the preliminary aeration must necessarily be conducted in a standard manner so as to eliminate this factor. The results of some experiments at room temperature by the aeration and evacuation method (described under 2b in appendix II) with typical new and used oils are given graphically in figure 6a. The foaminess is expressed in terms of the average life of the foam L_f , which is obtained by the methods described in this appendix and in appendix II. In this particular case, L_f is roughly half the time required for the foam to collapse completely.

Figure 6b presents some preliminary room temperature results obtained by beating and evacuation (method 2a of appendix II) with the same oils. The values by this method are now superseded by the more accurate ones in figure 6a (these agree well with those obtained by other methods - see table V), but the former data are included because of their interest in connection with the influence of water. The evacuation is conducted at a pressure well below the vapor pressure of water; hence, large amounts of vapor are produced by sometimes almost explosive evaporation of any moisture present. This leads to a voluminous foam, but one, in general, not as stable as an air foam produced by evacuation. On the other hand, in bubbling methods (e.g. method 3a, appendix II), where violent evaporation is not a factor, the presence of water has little influence on the stability of the foam produced.

For more detailed study of the characteristics of oil foam it was found desirable to resort to more elaborate

methods and apparatus, so that the collapse and drainage curves could be recorded simultaneously. For this purpose the Towne test was found satisfactory at room temperature, and the sintered glass bubbler at higher temperatures. Both of these methods are fully described in appendix II under methods 1c and 3b, respectively. In general, the form of the collapse and drainage curves vary widely with temperature and the oil being tested, and it is therefore advantageous to express foaminess in units which depend neither on analytic expression nor mathematical similitude of the curves. Convenient units which may be determined graphically are the average life of gas in the foam L_g and the average life of liquid in the foam L_l .

$$L_g = \frac{1}{g_0} \int_0^{\infty} g \, dt = \frac{1}{g_0} \int_0^{t_0} t \, dg$$

$$L_l = \frac{1}{l_0} \int_0^{\infty} l \, dt = \frac{1}{l_0} \int_0^{t_0} t \, dl$$

where g_0 and l_0 are the initial volumes of gas and liquid in the foam and g and l the volumes at the time t . The quantities L_g and L_l are not, in general, equal. From their ratio some information may be obtained concerning the relative importance of drainage and of film collapse. If an antifoaming agent is present, L_l is often greater than L_g ; that is, the films break more rapidly than the liquid can drain away. For a normal oil, however, $L_g \geq L_l$; that is, drainage proceeds for a time before the films break. In some cases it is desirable to express the foaminess as a single number. For this purpose the average life of the foam as an entity is useful L_f defined by an equation analogous to those for L_l and L_g , using the total foam volume instead of gas or liquid volumes. A further useful concept is the relative foam density d as defined by

$$d = l/(l + g)$$

As might be expected, the four quantities defined in the foregoing are not independent but are related by the equation

$$L_f = L_g + d_0(L_l - L_g)$$

where d_0 is the initial relative foam density.

Although the absolute value of the units as defined in the foregoing will vary with the type of apparatus, the data given in table V indicate that the ratio of the units for any two oils is not greatly affected by the method of testing. Minor discrepancies may be expected, since film characteristics would be somewhat different for widely different methods of making the foam to be studied, but from the data in table V, in which L_g is given for a number of oils by several methods at both room temperature and 100°C , it can be seen that there are no violently discordant results.

In table VI the results at room temperature by the Towne test for 13 different oils are given. Column 5 of the table gives the ratio of L_f to L_g . All these oils are of about the same viscosity (120 grade) except the Barton-Grimsley and the Squibbs medicinal oil; under these circumstances the ratio of the two lifetimes decreases regularly as the stability of the foam increases, as would be expected from considerations pointed out previously. In the case of the two most unstable foams, Union and Texaco, the fact that the ratio of L_f to L_g is greater than unity leads to the conclusion that an antifoaming agent is present and operative at room temperature. This conclusion is corroborated, at least in the case of Texaco, by data in connection with the influence of temperature on foam stability. The variations in foam stability of different oils of the same grade are not large in an absolute sense, most of the oils falling in the range of L_f between 45 and 85 minutes. In addition to the two oils of remarkable instability outside of this group, there are two oils giving extraordinarily stable foams, RPM Aviation and Shell Formula II. These oils are not supplied for military aviation, however, and their bad foaming characteristics are due to an additive. This additive apparently segregates in the froth, since it has been found (see appendix VII) that after a part of the oils has been foamed away, the residue behaves like the more typical aircraft oils, such as Aeroshell.

Effect of temperature on foaminess.— It is universally recognized that the foaming characteristics of lubricating oils change rapidly with temperature, consequently it was necessary to investigate the oils at elevated and intermediate temperatures, both pure and with added agents present. For this purpose a bubbler type of foam meter (3b in appendix II) was employed, kept at constant temperature

TABLE V.—COMPARISON OF FOAM TESTS

Average life of gas in the foam expressed in minutes (L_g)						
Temperature	Room			100° C		
Method	1c	2b	3b	2b	3a	3b
Union SAE 60	18.5	0.14	—	.38	1.8	1.1
Texaco 120	22.3	5.3	—	.64	—	—
Squibbs mineral oil	—	4.6	—	—	—	—
Texaco 120 (Moffett Field)	27.3	1.9	1.3	.58	2.2	1.0
NACA reference oil 120	51.5	7.8	25	.49	1.7	1.0
Texaco 120 (Used 24 hours)	61.3	9.7	—	.62	—	2.2
McClellan Field 120 (Used)	65.5	7.8	—	.62	—	—
Gulf Airline 120	71.8	9.5	33	.70	—	1.1
Barton-Grimsley	79.1	9.0	—	.57	—	—
Aeroshell 120	79.2	10.2	32	.54	1.3	2.0
McClellan Field 120	91.4	8.2	—	.78	—	—
Standard Aviation 120	103.6	11.7	55	.80	1.4	2.2
Shell Formula II	2056	60.2	—	6.6	—	>>10
RPM Aviation 120	4920	40.2	—	6.6	—	>>10

Method 1c Towne Test, arranged in increasing order for room temperature

2b Aeration and evacuation

3a Porous stone bubbler

3b Sintered glass bubbler

TABLE VI.— AVERAGE LIFETIMES AT ROOM TEMPERATURE
BY THE TOWNE TEST IN INCREASING ORDER

	L_f (min)	L_i (min)	L_g (min)	L_i/L_g (min)
Union Oil SAE 60	20.2	21.5	18.5	1.16
Texaco 120	25.7	30.2	22.3	1.35
Texaco 120 (Moffett Field)	28.4	29.7	27.3	1.08
NACA reference oil 120	46.9	41.6	51.5	.808
Used Texaco 120 (25 hr)	50.8	39.6	61.3	.647
Used McClelland Field oil 120	56.1	44.0	65.5	.672
Gulf Airline 120	57.8	40.0	71.8	.557
Aeroshell 120	64.1	45.2	79.2	.571
McClelland Field 120	74.4	52.2	91.4	.571
Barton-Grimsley	78.4	76.6	79.1	.968
Standard Aviation 120	85.9	58.9	103.6	.569
Shell Formula II 120*	1535	905	2056	.440
RPM Aviation 120*	2745	699	4920	.142

*These two are the only oils in the list definitely known to contain additives. They were tested without any defoamer such as is now often added by manufacturers. Later work will include values for the present day products.

by a vapor bath. The results obtained with some typical aeronautical oils as well as with some white medicinal oils at a series of temperatures are compiled in table VII. From these data it can be seen that the foam stability of a given oil diminishes about thirtyfold between room temperature and 100° C. At the latter temperature the variations in stability of different oils of the same viscosity is even less than at room temperature, the unstable classification having disappeared, although Standard RPM and Shell Formula II retain their remarkable foam stability. (See table V.) The white oils tested vary considerably in foam stability and are all much less stable than the aeronautical oils; that this, however, is due largely to viscosity changes will be shown later. Castor oil, on the other hand, is quite different from the mineral oils — the viscosity is about the same as a 120-grade oil, but the stability of its foam is much less. At the present state of knowledge, no definitive explanation of this behavior is possible, although it supports the hypothesis that viscosity of oil in the neighborhood of the surface is not that of oil in bulk.

In figure 7a, L_g is plotted against the temperature in degrees centigrade for Aeroshell 120, Squibbs mineral oil, NACA reference oil, and Texaco 120 (from Moffett Field). The rapid change of foaminess of aeronautical oil with temperature is at once apparent.

Much more interesting from a theoretical point of view is the method of presentation of the same results in figure 7b in which the logarithm of the average life is plotted against the reciprocal of the absolute temperature for the same oils. Data from the report of T. P. Hughes (reference 21) on Aeroshell 80 and B.P. Mineral oil are also included. Neglecting for the moment the anomalous results with Texaco 120, Moffett Field (which differed from other Texas aeronautical oils), it can be seen that the oils give excellent straight lines which are nearly parallel on this type of plot; that is, the foaming characteristics of these lubricating oils is well represented between room temperature and 100° C by a function of the form

$$L_g = A e^{B/T}$$

From these results it follows that it cannot be expected that a "critical" foaming temperature will be found

TABLE VII.- EFFECT OF TEMPERATURE ON THE FOAMINESS OF OILS

[Lifetimes given in min.]

Temperatures-	26° C			46° C			56° C			64.5° C			78° C			100° C			117.5° C			
	L _f	L _l	L _g	L _f	L _l	L _g	L _f	L _l	L _g	L _f	L _l	L _g	L _f	L _l	L _g	L _f	L _l	L _g	L _f	L _l	L _g	
BKH Mineral Oil	1.0	0.95	1.0	.3	.3	.3	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
McKesson Mineral Oil	4.1	3.9	4.1	1.14	1.06	1.16	.66	.61	.67	.39	.29	.43	---	---	---	---	---	---	---	---	---	---
Castor Oil U.S.P.	5:37	4.35	5.55	3.7	3.7	3.7	1.4	1.3	1.4	---	---	---	---	---	---	---	---	---	---	---	---	---
Union SAE 60	---	---	---	5.1	4.0	5.6	5.8	4.8	6.0	4.3	3.8	4.4	2.6	2.2	2.7	1.10	0.9	1.15	1.1	0.8	1.1	---
Squibb Mineral Oil	6.8	5.75	7.1	---	---	---	1.2	1.05	1.2	---	---	---	---	---	.47	---	---	---	---	---	---	---
Texaco 120 (Moffett)	---	---	1.3	1.9	2.3	1.8	4.0	4.0	4.0	---	---	---	2.0	2.0	2.0	1.0	1.0	1.0	---	---	---	---
NACA Reference Oil 120	---	---	25	9.7	8.0	10.0	6.0	6.0	6.0	---	---	---	2.5	2.5	2.5	1.1	1.1	1.1	---	---	---	---
Gulf Airline 120	---	---	33	11.1	9.0	11.5	6.9	6.0	7.0	4.7	3.9	4.8	2.2	1.85	2.25	---	---	1.1	.48	.40	.50	---
Aeroshell 120	29.5	18.3	32	---	---	11.0	6.9	5.3	7.2	---	---	---	2.9	2.3	3.0	1.10	0.8	1.15	---	---	---	---
Standard Aviation 120	---	---	55	16.5	9.8	17.5	10.0	6.4	10.5	6.2	4.2	6.5	3.2	2.3	3.4	1.7	1.25	1.8	0.8	0.8	1.1	---

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above which the oil will not foam. The influence of temperature upon the Texaco oil from Moffett Field is in striking contrast to the other oils. In general, the foaminess of an oil would be expected to decrease with rising temperature, as a result of decreasing viscosity and film strength, as is observed in the case of normal lubricating stocks and mineral oil. On the other hand, the situation is complicated if there is an antifoaming agent present, since it is quite easy to find substances serving as excellent antifoamers at room temperature, but totally ineffective at higher temperatures. If these circumstances prevail, the phenomenon of an increase of foaminess may be noted; the results with Texaco appear to be due to this cause. The similarity between the Texaco and another lubricating stock containing an antifoam is brought out in figure 8 in which Texaco, Aeroshell, and Aeroshell containing 0.11 percent Alronol are compared. In the case of both the Texaco and Aeroshell plus Alronol it can be seen that there is a remarkably sharp change in the foaming characteristics at about 50° C. Above this temperature the oil foams "normally"; the foam density is about 0.2 and independent of temperature. Below 50° C the foaminess is greatly reduced; and this antifoaming action is accompanied by an increase in foam density (to about 0.5) and, since the liquid laminae break more rapidly than the oil can drain away, $L_l \rightarrow L_g$. (See likewise fig. 10.) The sample of Union SAE 60 tested showed similar behavior. Since the full history of the latter oil is known, it can be said with some degree of certainty that in this case at least the defoaming action at room temperature arises from some process inherent in the refining, and not from added dopes.

Influence of viscosity on foam stability.— The kinematic viscosity of a number of lubricating and white oils was determined in the temperature range of interest by means of a Saybolt Universal viscosimeter. Conversion of the results from Saybolt Seconds to centistokes was made following the A.S.T.M. tables D446-39. In figure 9a values of L_l are plotted against the kinematic viscosity. Only the normal oils are included and mineral oils, such as Texaco and Union, which have an exceptionally low foam stability in a limited range, as well as the exceptionally persistent RPM Aviation are omitted. From the figure it is evident that the primary factor influencing the average life of the liquid in the foam, L_l , of undoped oils is the viscosity, since all the points lie within a few percent

of the dotted line, although some definite secondary tendencies are evident. The importance of this result lies in the fact that it shows that the foam stability of a good aircraft engine oil is about the same as a highly refined white oil of corresponding viscosity. From figure 9b it can be seen that L_f also is primarily dependent on the viscosity. Here, however, the oils fall more definitely into groups: Standard Aviation forms the most stable foam, Gulf Airline and Aeroshell fall in an intermediate classification, and NACA reference oil and the white oils form the least stable foam. This splitting into groups may be interpreted as evidence for Standard Aviation having the greatest film strength and the white oils the least. The difference in film strength naturally would be reflected in L_1 as well as L_f , but to a much smaller extent.

Independent evidence for classifying the oils into groups of different film strength may be adduced from data on relative foam density. During the collapse of a column of foam, the density varies from the top to the bottom, and also, in general, with the time, as drainage proceeds. What is calculated from data on foam height is an average density at any given time; if this average is plotted against the volume of liquid in the foam and extrapolated to zero volume, the value obtained may be regarded as the density at which the foam breaks. For a given bubble size the limiting foam density is proportional to the film thickness at which the foam breaks, and hence, is an inverse measure of the film strength. Limiting relative foam densities for the same oils that are depicted in figure 9 are given in table VIII.

From the data in table VIII, it is evident that the foam densities group themselves as would be predicted from the graph of L_f against kinematic viscosity: Standard Aviation lowest, Gulf and Aeroshell next, and NACA and the white oils the highest. A further and somewhat surprising result is that for these oils the limiting foam densities are virtually independent of temperature. The data are taken from runs with the bubbler-type foam meter; a similar extrapolation from data given by the Towne test at room temperature gives a like grouping, although the foam densities are slightly different in absolute magnitude, as might be expected because of the different bubble size.

TABLE VIII.- LIMITING RELATIVE FOAM DENSITIES

	46° C	56° C	78° C	100° C
Squibb mineral oil	—	0.13	0.13	—
BKH mineral oil	0.12	—	—	—
McKesson mineral oil	.12	.13	—	—
NACA reference oil 120	.12	.13	.13	—
Gulf Airline 120	.06	.07	.08	—
Aeroshell 120	—	.07	.02	.07
Standard Aviation 120	.02	.03	.05	.05

TABLE IX.- SURFACE TENSIONS AT 25° C

Oil	Tensiometer reading
Standard Aviation (120)	34.3
RPM Aviation (120)	34.5
Sinclair GX (120)	34.1
Gulf Airline (120)	34.0
Used Oil (Texaco 120)	34.2

TABLE X.- INTERFACIAL TENSIONS AND SLOPE OF I.T.
AGAINST TIME CURVES AT 2 MINUTES

Room temperature		
Oil (New)	I.T.	Slope (negative)
Aeroshell 120	42.1	0.66
Gulf Airline 120	47.5	0 approximately
Wolf's Head 120	31.6	0 approximately
McClellan Field New 120	39.5	0 approximately
Texaco (Moffett Field)	45.7	0 approximately
NACA reference 100	41.2	0 approximately
Standard Aviation 120	45.7	0.1
Texas Co. Navy Spec. 1120	45.7	0. approximately
(Used)		
McClellan Field Used	17.4	1.66
Texaco 120 (Moffett Field, 7½ hr)	31.6	.38
Texaco 120 (Moffett Field, 25 hr)	29.3	.37

Other Surface Properties

Surface and interfacial tensions.— The surface and interfacial tensions of some new and used aviation oils were determined at room temperature, using the Cenco-DuNuoy tensiometer, and a platinum ring 4 centimeters in circumference. The surface tensions of six oils were nearly the same, although they differed greatly in their foaming properties. A table of the surface tensions (uncorrected but comparable) is given in table IX.

The interfacial tensions were determined at the oil-water interface, using conductivity water. A change of interfacial tension with time was observed in some cases; so a method was devised for determining interfacial tension against time curves in order to obtain a more complete picture of the differences in the oils. The ring was immersed in the water layer, and the oil poured over, time being counted from the moment of contact between oil and water to rupture of the interface at a given tension.

A preliminary series of determinations of interfacial tension-time curves of some typical new and used oils is summarized in table X. In the table, values are given for interfacial tensions after 2 minutes, as well as the slope of the curve at that time, negative because the interfacial tension always decreased with time. Ring corrections were applied following Zuidema and Waters (reference 31).

These data give definite indication of a slow migration of some substance to the interface for all the used oils and new Aeroshell and Standard Aviation. The reduction in foaming ability of Aeroshell by prolonged contact with a large surface of water, described in appendix VII, is of interest in this connection.

The interfacial tensions quoted in table X are at pH 7. The interfacial tension of a white oil (Squibb) was found to be 42 dynes independent of pH from pH 2 to pH 11; in contrast, the aircraft lubricating oils tested (Aeroshell, Texaco, and Gulf) showed a reduction of several dynes when the solution was made alkaline, although the interfacial tension was nearly independent of pH on the acid side. This presumably is due to formation of sodium naphthenate soap with the alkali. Addition of a defoaming agent 0.001 percent EO-2, to Aeroshell largely removed the reduction of

interfacial tension at the alkaline water-oil interface, without affecting its value in acid or neutral solutions. The same defoaming agent 0.001 percent BO-2 lowered the interfacial tension of the white oil 6.5 dynes - also independent of pH, as is the case with the pure oil. On the other hand, 0.5-percent BO-2 lowers the surface tension of Aeroshell by the very large amount of 8.9 dynes.

Surface viscosity.- This is a property which has been claimed to be closely connected with foam behavior (of reference 9). The definition of surface viscosity, applied to liquid systems without floating films, has not been clearly made. The effect sought, however, was evidence of a frictional drag exerted on a measuring device in a thin-surface region, when there is a velocity difference between the device and the surface.

The instrument used consisted of a small platinum (tensiometer) ring supported on the lower end of a glass torsion fiber. A 1-rpm synchronous motor rotated a 10-centimeter-diameter dish containing the oil on a small turntable directly under the ring. The ring was lowered until it just touched the surface and then slowly raised by means of a screw device on the support for the torsion fiber. The angular deflection produced on the ring by the frictional drag of the liquid was measured by a galvanometer scale reflected in a mirror rigidly attached to the ring.

For two oils at 25° C, Aeroshell 120 and Texaco 120, the curves of deflection against vertical distance of the ring from the point of first contact were identical, and the deflection became zero before the oil surface ruptured, thus giving no evidence of a "surface" viscous drag. It is evident that this method does not sufficiently separate surface viscosity if any from bulk viscosity. Further measurements will be made on torsion of annular films between two concentric rings.

Demulsibility tests on existing aeronautical oils.-

A series of experiments were carried out to investigate the possibility of a relation between the rate of demulsification of a water-oil emulsion and foaminess of the oil. In crude room temperature experiments in which the oil and the water were shaken together by hand and the rate of demulsification noted, the stability of the emulsion paralleled qualitatively the foam stability of the five

oils tested, Union SAE 60, Texaco 120, NACA reference oil 120, Aeroshell 120, and RPM Aviation 120. No correlations were observed, however, with high-temperature steam emulsification of these same oils by A.S.T.M. Method D 157-36. One experiment with oxidized Aeroshell showed an enormous increase in emulsion stability over the new oil, which found no counterpart in increased stability of foam.

Analysis of oils.— Analyses on new and used Texas oils have been carried out by the Shell Development Company, in which the following results were obtained:

1. New Texas oil
2. Used Texas-Navy Spec. 1120 - First Sample
3. Used Texas-Navy Spec. 1120 - Second Sample

	<u>(1)</u> (percent)	<u>(2)</u> (percent)	<u>(3)</u> (percent)
Water (Fischer)	0.00(5) .00(5)	0.00(6) .00(6)	0.00(8) .00(9)
Isopentane insolubles 15/1	.10, .10	.19, .20	.56, .54
Specific gravity 60/60° F	.882	.884	.884
Acid neutralization No. by (A.S.T.M. D664-42T) mg. KOH/g	.0(1)	.1(4)	.2(5)
Saponification No. by (E47-40) mg. KOH/g	.(3)	.(9)	1.(1)
Strong acid Saponification No. (E47-40) mg. KOH/g.	.(1)	.(1)	.(1)
Base saponification No. (E47-40) mg. KOH/g.	.(0)	.(0)	.(0)
Ash	less than .00(1)	.07(2) .07(0)	.12(0) .12(0)
Lead (gravimetric)	————— —————	.06(3) .06(1)	.08(3) .08(2)

	<u>(1)</u> (percent)	<u>(2)</u> (percent)	<u>(3)</u> (percent)
Copper (colorimetric)	=====	0.0007(2) .0007(2)	.0010(0) .0010(0)
Iron (colorimetric)	=====	.003(3) .003(3)	.009(2) .009(2)

Spectrographic Analysis

(Estimated percentages of inorganic
portion—not determined amounts.)

	M.C. (percent)	M.C. (percent)
Lead	1.	1.
Iron	.1-1	.1-1.
Aluminum	.1-1.	.1-1.
Copper	.1-1.	.1
Calcium	.01-.1	.01-.1
Tin	.01-.1	.01-.1
Zinc	.01-.1	.01-.1
Silver	.001	.1

Chromium, magnesium, manganese, nickel, cadmium, and cobalt were also found in samples (2) and (3) but not exceeding 0.01 percent (estimated) in any case.

In this laboratory lead analyses have been made on these same oils by Lindquist. The results show a somewhat higher percentage of lead. For the used oil reported as (2) by the Shell Development Company, the total lead obtained (including volatile lead) was 0.16 and 0.14 percent (av. 0.15 percent).

Samples of oil have also been analyzed for water according to A.S.T.M. D95-30. No determinable water (less than 0.05 percent) was found for the following oils:

Aeroshell 120

New Texas-Navy Spec. 1120

Used Texas-Navy Spec. 1120 - First Sample (Moffett Field)

Used Texas-Navy Spec. 1120 - Second Sample (Moffett Field)

Used Oil (McClellan Field)

Of significance in the foregoing reported analyses are the following factors:

1. The acid neutralization number becomes markedly increased when the oil is used.
2. Used oils contain a relatively large quantity of metals, of which lead is the principal constituent in the samples tested. If volatile lead compounds are present, it has been shown that the total lead can be as much as 0.14 percent of the oil.
3. The quantity of water present in used oils (or new oils) is definitely less than 0.1 percent and probably less than 0.01 percent.

Summary

Foaming characteristics.— The foam stability of a number of typical new and used aeronautical oils was measured and compared at room temperature, as well as at 100° C, by several methods in current use. Intermediate and higher temperatures were investigated by a bubbler type of foam meter, in which both aeronautical and white oils were tested.

In general, a decrease in foam stability accompanies a rise in temperature. As an example, by method 3b (appendix II), the average life of the foam of Aeroshell 120 is 30 minutes at room temperature, and 1.1 minutes at 100° C.

A Texas oil and a Union oil are exceptional in that the foam stability is markedly low at room temperature, but sharply increases at 50° C and 40° C, respectively, to values comparable with other oils at the same temperature. A similar behavior is shown by Aeroshell 120 when certain antifoaming agents are present.

The primary factor influencing the relative foam stability of most undoped aeronautical and white oils, is shown to be the kinematic viscosity. Methods for evaluating secondary factors, such as film strength, are indicated.

Other properties.— Surface and interfacial tensions (against water) are given for several oils, as well as the influence of pH on the the latter. An attempt to demonstrate surface viscosity on the bulk oil was unsuccessful, as were efforts to correlate steam emulsification (A.S.T.M. Method D 157-36) with foam stability. Chemical analyses of typical new and used aeronautical oils are recorded.

APPENDIX IV

SURVEY OF THE EFFECTS OF CHEMICAL AGENTS ON OIL FOAMING

Introduction

The chemical aspect of the problem of oil-foaming in airplane engines was approached by trying numerous types of available chemicals to determine their effect upon the foaming of the oil. In a field nearly devoid of theory, this procedure furnished a background of experience which is summarized in the tables of this section. The chemicals available for the survey consisted principally of McBain's collection of detergents and related materials. Although many of these are available only under trade names, the chemical constitution of most of them is known, with some information as to the degree of purity. Many of them are known to be mixtures. Other agents of interest have been tried as they were suggested and became available.

The outstanding results of the survey as regards the discovery of chemical antidotes for the foaming problem may be stated briefly.

The experiments in this appendix concern commercial materials and pure chemicals; the results with two pure chemicals added together also are discussed in appendix V. Only two members of the former group satisfactorily fulfill the requirements for an antifoamer under all of the test conditions here used. These were designated as BO-1 and BO-2. Many other materials or chemicals were found which were very satisfactory at room temperature, especially in the presence of moisture. Some forty of these are listed in table XII, but as shown in table XI, most of them became completely ineffective at temperatures of 100° C or above, and all of them, except BO-1 and BO-2, which show activity at 100° C ceased to be effective when all water evaporated.

Agents compounded from "simple" substances have shown tremendous promise as satisfactory antifoamers under all of the test conditions. Four of these are outstanding, although not necessarily the ultimate to be expected: Glycerol with Aerosol OT; glycerol with lead Aerosol OT; glycerol with calcium Aerosol OT; and glycerol with octyl

tripolyphosphate. Diethylene glycol has been used with some success in place of glycerol, as have Sapamine MS and triethanolamine with a lesser effectiveness.

The results of the survey in terms of progress in theory are at least equal in significance to the finding of some acceptable antidotes. The extreme importance of water in the antifoaming action has led to experiments that suggest a reasonably satisfactory mechanism for some antifoaming action. The successful use of glycerol (and similarly diethylene glycol, Sapamine MS, and triethanolamine) and the nonspecificity of the agent used with the glycerol have suggested that it is the essential antifoamer, while the other agent is simply a dispersing agent. (See appendix V for the development of this hypothesis.) The role of the degree of dispersion is now recognized as being so important that the contents of these tables must be regarded as a primitive survey in which only gross effects were observable. Certain apparent discrepancies in the tables are due to the exploratory nature of the tests; however, most of them have been experimentally worked out or are discussed in the section of this appendix entitled, Discussion.

Arrangement of tables.— The test data have been classified into five tables; tables XI through XIV contain tests of simple agents including commercial materials, many of which are mixtures, and table XV those of compounded agents. The tests of simple agents were so numerous that they were subdivided according to the results of the test, with the more interesting substances listed in tables XI and XII, and the less interesting ones in tables XIII and XIV. All substances showing antifoaming action on oils at 100° C are listed in table XI, because almost always, if a material is effective at 100° C, it is also operative at room temperature. Only those showing exceptional antifoaming ability at a lower temperature are listed in table XII, and all others with some antifoaming action are listed in table XIII. Table XIV lists all compounds tested that showed little effect on foam stability or were stabilizers. The compounded agents, table XV, are not subdivided, but are listed alphabetically by the waterlike or glycerol-like component, arbitrarily in cases of doubt.

Material in tables.— Where possible, the results of multiple tests upon the same substance have been combined into a single line in the table. The name of the substance,

the source from which it was obtained, its behavior as an antifoamer, the temperature and concentration at which it was tested, the method by which it was tested and in which oils, and other pertinent remarks are indicated for each. All concentrations are in percent by volume, and generally are approximate. All temperatures are in degrees centigrade. The source of material, behavior as an antifoamer, test method and oils tested are abbreviated by the use of code letters and numbers. The keys to the codes are given in the pages immediately following the tables. The code designation is given in parentheses after all references to grade, test method, and oils in the text of this appendix.

In table XV, under "Remarks," are listed "Concentrate" numbers and "B-10" and "B-110" numbers. These refer to the serial designations of certain mixtures, and are included for cross reference to the test file.

KEYS TO CODES USED IN TABLES

Grades of Antifoamers

- A. No foam by bubbling methods. Collapse in a few seconds by other methods.
- B. Foaming reduced to approximately 1/5 of original.
- C. Foaming reduced to approximately 1/3 to 1/2 of original.
- D. Foaming reduced by less than 1/2 of original.
- E. No effect.
- F. Foam stabilized.

Oils Tested

- | | |
|----------------------------|---------------------------------------|
| 1. Aeroshell 120 | 7. Texaco 120 (from Moffett Field) |
| 2. Gulf 120 | 8. Aeroshell 120, Laboratory Oxidized |
| 3. McClellan Field New 120 | 9. Moffett Field Texaco 120, Used |
| 4. NACA reference 120 | |

- | | |
|--------------------------|-------------------------------|
| 5. Standard Aviation 120 | 10. McClellan Field 120, Used |
| 6. RPM Aviation 120 | 11. Shell Formula 2 |

Test Methods

(Refer to appendix II for complete descriptions)

- | | |
|---|--|
| 1d. Test-tube shaking | 3aa. Bubbling in column with porous ball no. 2 |
| 2a. Beating and evacuation in 200 ml. flask | 3b. Bubbling in column with sintered glass |
| 2b. Aeration and evacuation | 3d. Bubbling in beaker with sintered glass |
| 2c. Evacuation in 200 ml. flask | 3e. Bubbling in column by Bikerman method |
| 3a. Bubbling in column with porous ball no. 1 | |

SOURCES OF AGENTS

1. Alox Corporation
2. Alrose Chemical Company
3. Amecco Chemicals, Incorporated
4. American Cyanamid and Chemical Company
5. American Lecithin Company
6. Atlas Powder Company
7. Beacon Company
8. Bitumels Asphalt Works
9. Carbide and Carbon Chemicals
10. Celluloid Corporation

11. Ciba Company
12. Columbia Chemicals Division, Pittsburgh Plate Glass Company
13. Commercial Solvents Corporation
14. Dow Chemical Company
15. DuPont Company, Chemicals Department
16. Eastman Kodak Company
17. Emulsol Corporation
18. Jacques Wolf and Company
19. General Dyestuffs Corporation
20. Glyco Products Company
21. Gulf Oil Company
22. Hart Products Company
23. Hercules Powder Company
24. Schering Kahlbaum A. G., Berlin
25. Laurel Soap Manufacturing Company
26. Marshall Dill, San Francisco
27. Metasap Chemical Company
28. Monsanto Chemical Company
29. National Aniline Division, Allied Dyes and Chemicals
30. Philadelphia Quartz Company
31. Procter and Gamble
32. Rit Products Company
33. Röhnm and Haas
34. Shell Development Company

35. Shell Oil Company
36. L. Sonneborn Sons, Incorporated
37. Standard Oil By-Products Laboratory
38. Stanford University Chemical Laboratory Preparation
39. Textile Chemical Products Company
40. A. H. Thomas Company
41. Universal Oil Products
42. Victor Chemical Works
43. T. C. Wilson Company

DISCUSSION

Attention again is called to BO-1 and BO-2 in table XI; and in table XV to glycerol with Aerosol OT, calcium Aerosol OT, lead Aerosol OT, or octyl tripolyphosphate; diethylene glycol with calcium Aerosol OT or lead Aerosol OT; Sapamine MS with Aerosol OT; and triethanolamine with triethanolamine oleate and lead Aerosol OT. These are the most successful antifoaming agents.

It is conspicuous that all the successful agents except BO-1 and BO-2 have been found effective only in the presence of water, glycerol, diethylene glycol, or similar compounds. The idea already has been mentioned (with reference to appendix VII) that these simple compounds are the real antifoamers; while the other components serve as dispersing agents. By this theory, BO-1 and BO-2 have the unique characteristics of being both effective antifoamers and self-dispersing materials. The inefficiency of the agents, glycerol, and so forth, when merely stirred into the oil, is shown in table XIV. Similarly, water (1 percent) when stirred into the oil, decreases the foaming only about one-fifth.

The role of the degree of dispersion in determining the effectiveness of simple agents has been further demonstrated by the behavior of 2-nitrol 1-butanol. Although recommended as an antifoamer by the Standard Oil Company,

the routine evaluation in this laboratory, in which it is stirred into the oil and tested at room temperature, showed it to be without effect. However, when the agent was dispersed by circulation through a gear pump or a colloid mill, it showed good antifoaming ability (B) at room temperature (table XIII). At 100° C the dispersed agent became a foamer (F). Other agents which might be effective if properly dispersed have been passed over; work in progress should uncover any serious errors in classification.

The behavior of dimethyl silicone (table XII) is less clear-cut as an effect due to degree of monomer dispersion. By the method of beating and evacuation (2a) at room temperature, dimethyl silicone showed no antifoaming action (E). However, the aeration and evacuation (2b) method showed it to be an excellent room temperature antifoamer (A). Samples were beaten as for method 2a, and aerated as for method 2b, and exchanged in the apparatuses. The beaten sample, evacuated in the 2b apparatus, showed no effect (E), while the aerated sample evacuated in the 2a apparatus was an efficient antifoamer (A-B). The discrepancy was thus proven to be due to the methods of pre-treatment, but whether the presence of finely divided air activated the agent or the violent stirring by the air dispersed it, or whether the method of evacuation in one case stretched the bubbles past their elastic limit (see appendix IV), is unknown.

In another experiment, BO-1 was shown to lose its effectiveness unless present in quantity in excess of its solubility. An oil (Gulf 120) that had been rendered completely nonfoaming by the addition of 0.01 percent BO-1 was set aside in a bottle for 3 months. At the end of that time, a portion was poured from the top, and tested for foaming by beating and evacuation (2a). The oil foamed considerably (antifoamer grade C). The oil sample was warmed and shaken and cooled again. The foam now collapsed in a few seconds (antifoamer grade A), the same as when the sample was originally made.

Relative reliability of test methods.— The most quantitative tests are the aeration and evacuation method (2b) and the porous ball bubbling method (3a, 3aa). Both of these have been shown to be reproducible on many repetitive trials over a long period of time. Beating and evacuation (2a) and evacuation alone (2c) are qualitative tests, and at 100° C are erratic due the short time of collapse

of foam of even an untreated oil (45 sec) in the test flask. In conflicts between these methods that have not been cleared up by repeated tests, methods 2b and 3a are favored over 2a and 2c. The beaker bubbling test (3d) is also qualitative, of intermediate reproducibility. It has the advantage of being continuous, allowing time for evaluation, and the disadvantage that the results cannot be expressed numerically.

Relative ease of defoaming of the oils.— The oils tested show great differences in the ease with which they may be defoamed (see also appendix III). Texaco (7) foams less at room temperature, but at elevated temperature (above 50° C), it behaves like the majority; that is, Aeroshell (1), Gulf (2), McClellan Field New (3), NACA reference (4) and Standard Aviation (5). RPM Aviation (6) is exceptional in that it foams much more than the others at all temperatures and is the most difficult to defoam. It has been shown to contain a separable foamer, in contrast to the others except Shell Formula II; the foamer appears to react unfavorably with otherwise successful foam inhibitors, notably B-10-186 (in table XV under glycerol). The used oils, in general, are more difficult to defoam than the corresponding new oils. In particular, they need larger amounts of antifoaming agent. There is considerable difference in the two samples of used oil included in the tabular data. The Moffett Field Used (9) is from an airplane engine in which serious bearing failure occurred, and the oil is very black and filled with grit and sludge. In this condition, it is exceptionally hard to defoam. A simple filtration renders it comparable to the other used oil. The McClellan Field Used (10) is only slightly darker than the unused oil; it is clean and responds well to the antifoamers that are the best for the new oils.

Temperature.— The phenomenon of a compound being an effective antifoamer at room temperature and without influence on the foaminess at 100° C is common. Several causes may be responsible.

1. The agent is destroyed at elevated temperature. Most of the compounds used are of sufficient stability to make this explanation improbable.
2. The agent is volatilized. This is known to occur when the compound has sufficient vapor pressure. Evaporation of water destroys the efficacy of many additives, as illustrated in tables XI and XII.

3. The character of a sorbed layer at the air-oil interface changes reversibly with temperature, with consequent changes in the film stability.
4. The agent may be soluble and dissolved at one temperature and insoluble or only partly dissolved at another temperature.

Alronol and sorbitol dilaurate are two substances that give a reversible temperature effect, and were chosen for more complete investigation. The results are presented graphically in figure 10 (L_g as the average lifetime of the gas in the foam). It can be seen that increasing the concentration of Alronol shifts the break in the curve toward higher temperatures. It was noted that at temperatures at which the Alronol was effective, the oil was hazy, as though some constituent were dispersed colloiddally rather than dissolved; above the effective temperature, the oil was optically clear. Sorbitol dilaurate behaved quite differently from Alronol, being remarkable in that between 40° C and 100° C there was almost no temperature coefficient of the foaminess.

Concentration.— The concentration in which an agent is added to the oil may determine whether it enhances or inhibits foaming. In general, high concentrations (over 1 percent) enhance foaming, even when lower concentrations may inhibit. Practical considerations of cost limit the range of greatest interest to about 0.1 percent or below, which fortunately appears to be an effective concentration for most substances that will inhibit foaming at all. Optimum concentrations have been found in certain cases; illustrative foam stability against concentration curves, using metallic soaps for examples, are reproduced in figure 11. These curves were obtained by the porous-ball-bubbling method (3a) at 100° C on Aeroshell 120 oil (1). Represented are the inactive-agent type (curve 1), with no inhibiting effect but an enhancing effect as concentration is increased; the type with a sharp optimum for inhibiting concentration (curve 2); and a complex type in which one or more foaming minimums and maximums may occur (curve 4).

As examples of agents with a sharp minimum in the foaming curve, the Spans and Tweens (Atlas Powder Co.) may be cited.

The data listed below were obtained by the aeration and evacuation method (2b) at room temperature on NACA reference oil (4).

Span 40 (percent)	Span 60 (percent)	Tween 61 (percent)
0.01 F	.05 F	.01 F
.10 A	.20 A	.05 A
.50 F	.50 F	.10 D(A with 2 per- cent water)
		.50 F

Thick films.— The formation of thick oil films has been observed after the addition of certain agents, notably glyceryl monostearate, Tergitol 08, Lamepon 40, Penatrol 60, and Span 40, to the lubricating oils. These films, because of their extreme durability and longevity, have been of particular interest. In a typical case, a foam may collapse at a normal rate initially, then at a slower rate, and finally become stable with the formation of thick, immobile films, which may extend clear across a 3-centimeter-diameter glass cylinder. Such a large film from oil containing dehydrated Penatrol 60 or Span 40 is so tough that it may be blown from the bottom to the top of the cylinder without rupturing, by introducing air beneath it. When this type of film ruptures, it does not burst suddenly in the usual way, but may tear slowly from a hole in the center that spreads outward and require several seconds to disappear. In general, these films—

1. Were of visible or macroscopic thickness and showed no signs of draining;
2. Remained immobile over a period of several hours;
3. Showed definite evidence of structure;
4. Could be stretched considerably without rupturing;
5. Supported solid, immobile particles in their surfaces;
6. Did not burst in breaking, but tore slowly.

FOAM INHIBITORS AT 100° C.

AGENT (SOURCE)	GRADE	CONC'N %	TEST METHOD	OILS TESTED	REMARKS
Aciterge OL (13)	C	.3	3a	1	F on continued bubbling
Antifrothing agent (17)	B	.5	2c	1	F without water, by 3a
Blendene (20)	B - C	.2	3aa	1	C without water
BO-1	A	.01-.02	3a	1, 7, 9	
"	A	.5	2b	4	
BO-2	A	.0002-.01	3d	1, 2, 7	A to 125° with 6, 200° with 7
Castor oil silicate (38)	A	.5	2c	1	F by 3a on oil 4
Diethyl lauryl amido phosphate (42)	A	.4	3a	1	F without water
Diethyl laureate (20)	A	.7	2a	1	
Dimethyl silicone (35)	C - E	.1-.9	2a 3aa	1	Small volume of stable foam
Ethyl silicate (9)	B - C	.1-.5	2b	1	See discussion of these results
"	D - E	.005-.14	3a	1	
"	A	.1-.5	2a	1	
Glyceryl monostearate (20)	C		2b 3a	1	D - F at higher conc'n
Lead Palmitate (38)	B - C	.1	2c	1	Grade depends on technique, A by 2a
Nonanol NR (29)	C	2.5	2c	1	F without water
Octyl tripolyphosphate (42)	A	.1	2a 2a	1	F after water boils away
Penetrol 60 (7)	A	.1-.5	2a 2b	1, 4	F after water boils away (3aa)
Tergitol penetrant 4 wax (9)	A	.2	3a	1	F after water boils away
Tetraoctyl pyrophosphate (42)	A	.1	3aa	1	C after water boils away
"	E	.2	3a	6	
Trioctyl tripolyglycol tetrapolyphosphate (42)	C	.2	2c	1	D at 25° C. by 2c
See also TABLE V					

Table XII

OUTSTANDING FOAM INHIBITORS IN THE LOW TEMPERATURE RANGE

AGENT (SOURCE)	GRADE	TEMP. RANGE	CONC'N %	TEST METHOD	OILS TESTED	REMARKS
Anterge OL (13)	A - E	26-78	.1-.5	2a 2b 3b	1, 4	Defoaming lessens as temp raised
Aironol (2)	A - E	26-100	.1-2.3	2b 3a 3b	1, 4	F above 60° C.
Ammonium Stearate (20)	A	Room	.3	2a	1	
Antifrothing agent (17)	A	25	.5	2c	1	
BO-1	A	Room	.01-.5	2a 2b 3a	1, 2, 4	
BO-2	A	Room	.0001	2b 3d	1, 4, 6, 7	
Butyl lauryl acid o-phosphate (42)	A	Room	.5	2c	1	
Calcium Aerosol OT (4)	A	Room	.7	2a	1	F without water
Copper Aerosol OT (4)	A	Room	.7	2a	1	F at 100°, .005-.14 by 3a
Copper palmitate (24)	A	Room	.05-.2	2a 2c 3a	1	F at 100°, .002-.06% by 3a
Diethyl lauryl amido phosphate (42)	A	Room	.1-.5	2b 2c	1, 4	
Diethyl laureate (20)	A	Room	.5-1.2	2a 3a	1, 2	
Dimethyl silicone (35)	A - B	Room	.05-1.2	2b	1, 4	
"	A - B	Room	.1	2a	4	Sample aerated previously by 2b
"	D - E	Room	.05-1.25	2a	1, 4, 5	See discussion of these results
Dioctyl stearyl amine pyrophosphate (42)	A	Room	.25	2c	1	B for oil 9, F at 100° C.
Dunonol OS (15)	A	Room	.1	2c	1	B with water
Emulsol 607 M (17)	A	Room	.5	2b	4	D at conc'n .1%; F at 100°
Ethyl silicate (9)	A	Room	.09	2b	4	
Foamex (20)	A	Room	.5	2a	6	F at 100°
Glyceryl monostearate (20)	A	Room	.15-.4	2a	8	
"	E	Room	.005-.5	2a 2b 2c 3a	1, 2, 4	C - F without water
Lead palmitate (38)	A	Room	.25-.5	2a	1, 8	
Lubrital (40)	A	Room	.5	2a 3a	1, 8	Effect on B decreases with time
Monolauryl acid o-phosphate (42)	A	Room	.25	2c	1	
Monolauryl dipolyglycol o-phosphate (42)	A	25	.1	2c	1	At 100° F by 3a, C by 2a
Monooctyl dipolyglycol o-phosphate (42)	A	25	.1	2c	1	D at 50°, F at 100°
Octyl tripolyphosphate (42)	A	Room	.1, 1	2a	1, 8	F without water
Orvus SS paste (31)	B	Room	.5	2a	1	With or without water
Orvus WA paste (31)	B	Room	.5	2a	1	With or without water
Penetrol 60 (7)	A	Room	.08-.5	2a 2b	1, 4	F without water
Phosphorated octyl amine (42)	A	Room	.1-.25	2a 3a	1	Question whether water necessary
Phosphorated stearyl amine (42)	A	Room	.1-.4	2a 3a	1	B for oil 9
"	A	Room	.2	3a	8	Oil must be filtered; otherwise F
Reagent 903 I	A	Room	.1	2b	1	C - D with less than .5% water
Sepamine WS (11)	A	25	.5	2c	1	With or without water
Sorbitol dilaurate (20)	A	Room	.2-.7	2a 3b	1	C at 46°, F at 100°
Tergitol 7 (9)	A	Room	.5-1	2a	1	F without water
Tergitol 08 (9)	A	Room	.02-.5	2b	4	
Tergitol penetrant 4 (9)	A	Room	.1-.5	2b	4	Agent contains water
Tergitol penetrant 4 wax (9)	A	Room	.0005	2b	4	F without water
Tributyl citrate (13)	A	Room	.5	2b	4	F at conc'n .1%
Trisethyl ricinoleate silicate (38)	A	Room	.1-.5	2b	4	
Tween 21 (6)	A	Room	.2	2b	4	F without water
Tween 22 (6)	A	Room	.5	2b	4	F without water, .05% at conc'n
Zinc Aerosol OT (4)	A	Room	.2	2a	1	C on oil 2, F on oil 1 at 100°
See also TABLE V						

LIMITED FOAM INHIBITORS

AGENT (SOURCE)	GRADE	TEMP. RANGE	CONC'N %	TEST METHOD	OILS TESTED	REMARKS
Aerosol 22 (4)	F	Room	.5	2a	1	F with 5% water
Aluminum palmitate (36)	C	Room	.5	2c	1	
2-Amino 1-butanol (13)	C - F	Room	1-.5	2b 2c	1.4	C at .1%, F at .5%
Antifoam BF (15)	C - F	Rm-100	1.1-.2.5	2b 3a	1.4	C at .5%, Rm temp. on oil 3
Beeswax	B	24	.5	2a	1	F at 100°
Beryl colloids (9)	B	Room	.7	2a	1	
n-Beryl phosphate (16)	C	Room	.5	2b	4	D at conc'n .1%
Candelilla wax	F	100	.05-.1	2b	7	A by 2a at 70°
Capryl alcohol (3)	F	Room	.5	2b	4	D at 100° by 2a on oil 1
Capryl laurylamine tripolyphosphate (42)	B	Room	.7	2a	1	F at 100°, conc'n .1%
Carnauba wax	F	100	.05	3aa	1	A by 2a at 90°
Cephalin (ox-brain) (5)	C	Room	.5	2a	1	F at 40°
Copper laurate (38)	B	Room	.25	2a	1	
Cupric acetate	C - D	Room	.7	2a	1	
Defoamer S-190-W (18)	F	Room	.05-.2	2b	4	R with .2% water
Diethyleneglycol monooleate (20)	C	Room	.7	2a	1	
Dialcyl dinaphthenate (20)	C	Room	.7	2a	1	
Dupont antirust (12)	C	25	.5	2c	1	Added water has no effect
Ethyl ether	C	25	1.	2c	1	
Ethyl oleyl glycol o-phosphate (42)	B	25	2.5	2c	1	
Ethyl phosphate (16)	A - D	Room	1.1-.5	2a 2b	1.4	Agent deteriorates. D at 100°
Ferric stearate (36)	C	Room	.5	2c.3a	1	
Glyceryl dioleate (20)	C	25	.5	2c	1	Added water has no effect
Lead laurate (36)	C	Room	.5	2a	1	F at 100° in conc'n above .05%
Mannide monooleate (20)	C	25	.5	2c	1	
Mercury palmitate (36)	C	Room	.5	2a	1	
Methyl lauryl acid o-phosphate (42)	B	25	2.5	2c	1	
Neoclene F (38)	B	25	2.5	2c	1	
Ninol no. 713 (35)	B	25	.5	2a	1	D at 100°
N-Nitro 1-butanol (57)	B	Room	1.1-.2	1d 2b	1	Mixed by colloid mill. Otherwise D
Penetrol 45 (7)	F - Y	100	1.1.5.1.	2b 3a	1.5	F when dispersed by colloid mill
Petronats (36)	C	Room	1.1.5	2b 2c	1.4	F at 100° by 2c on oil 1
Polyglycerol ester	C - D	Rm.100	1.	2c 3aa	1	A in presence of petroleum ether
Frestone antifreeze (9)	C - D	Room	1-20.	2c	1	
Pyrophosphatidic acid (42)	C	25	.25	2c	1	
Sodium hydroxide (aqueous)	C - D	Room	.25	2b 2c	1	
Sodium-potassium alloy drying agent (36)	C	Room		2c	1	
Span 40 (6)	A - F	Room	.01-.5	2a 2b	1.4	See discussion of Spans & Tweens
Span 60 (6)	A - F	Room	.02-.5	2b	4	A only at conc'n .1%. F at 100°
Sulphonated castor oil (23)	C	Room	.1	2b	1	Added water has no effect
Tetraoctyl pyrophosphate (42)	B	Room	2.5	2c	1	
Tributyl phosphate (15)	C	Room	1.1.5	2b	4	
Triethanolamine (9)	C	Room	.02-.5	2b	4	Not effective after heating
Turkey red oil (19)	C	Room	.5	2b	4	D - F without water
Tween 61 (6)	A	Room	.05-.09	2b	4	F after standing several hours
" " "	F	Room	.02-.5	2b	4	
" " "	A	Room	.1	2b	4	In presence of .2% water
Yelkin C (5)	C	Room	.25-.5	2a	1	
Zinc palmitate (36)	C	Room	.7	2a	1	

Table XIV

FOAM ENHANCERS AND NON-INHIBITORS

AGENT (SOURCE)	GRADE	TEMP. RANGE	CONC'N %	TEST METHOD	OILS TESTED	REMARKS
Aerosol DGA (4)	F	100	.1	2a	1	
Aerosol CT (4)	F - F	100 Rm	1.1.5	2a	1	
Alkyl oxalohexanoate	F	Room	.5	2a	1	Slight defoamer with 2% water
Alkyl oxalohexanoate	F	Room	.7	2a	1	Slight defoamer with 2% water
Alox 100 (1)	F	100	.1	2a	1	
Alox 400 (1)	F	100	.1	2a	1	
Alox 500 (1)	F	100	.1	2a	1	
Amazo BB ester (5)	F	Rm-100	1.1.5	2a 2b	1.4	
Amazo BB wax (3)	F	Rm.100	1.1.3	2a 2b	1.4	
2-Amino 2-ethyl 1,3-propanediol (18)	F	Room	.5	2c	1	
2-Amino 2-methyl 1-propanol (15)	F	25	.5	2c	1	
Anthracene (24)	D	40	.05	2a	1	
Ammonium acetate	F	Room	.1	2b	4	
Antifoam LF (16)	F	Rm.100	1.1.5	2a 2b	1.4	
Antifoam LFX (16)	D - F	Room	1.1.5	2b	4	Added water has no effect
Antifrother 3769A (17)	F	100	.2	3aa	1	
Antifrother 3769B (17)	F	100	.1	2a	1	
Antifrother 3769C (17)	F	100	.1	2a	1	
Antifrother 3769D (17)	F	100	.1	2a	1	
Aquasol AR (755) (4)	F	Room	1.1.5	2b	1	Added water has no effect
Bloom asphalt (1-20) (34)	F	Room	.1	2b	1	
Barium palmitate (36)	F	Room	.5	2a	1	
Benzoic acid	F	Room	.25	2a	1	
Benzylamine	F	Room	.25	2a	1	
Beryl acetate (9)	F	Room	.7	2a	1	
4-tert-butyl catechol (16)	F	Room	.7	2a	1	
Beryl calcium laurate (20)	F	Room	.7	2a	1	
Calcium palmitate (36)	F	Room	1.1.5	2a 2b	1.4	Added water has no effect
Camphor	F	Room	.1	2b	4	
n-Caprylic acid	F	25	.5	2c	1	
Carbitol palmitate (20)	F	Room	.7	2a	1	
Cationic Agent A (42)	F	Room	.7	2a	1	

AGENT (SOURCE)	GRADE	TEMP. RANGE	CONC'N %	TEST METHOD	OILS TESTED	REMARKS
Cationic Agent "B" (42)	F	Room	.7	2a	1	
Cationic Agent "C" (42)	F	Room	.7	2a	1	
Chemical Captain (41)	F	Room	.7	2a	1	
Chemical Sergeant (41)	F - F	Room	1.5-.7	2a 2b	1.4	
Chloral hydrate	F	Room	.25	2a	1	Added water slightly stabilizes
Cholesterol (16)	F	Room	.1	2b	4	
Cholesteryl palmitate (16)	F	Room	.1	2b	4	
Cobalt stearate (27)	F	Room	.05	2b	1	Added water has no effect
Copper oleate	F	Room	.5	2a	1	
Crotylic acids, 220° - 240° (8)	F	Room	.7	2a	1	
Dibutyl phosphate (13)	F	Room	1.5	2b	4	
Diethanolamino ethyl phosphatidic acid (42)	F	Room	.5	2c	1	
Diethylene glycol (16)	F	Room	1.5	2b	4	
2,4-Dimethyl 6-ter-butyl phenol (34)	D - F	Rm.100	1.5	2b 3a	1.4	
Dipropyls	F - F	Room	.05-.1	2c	1	
D.N. Emulsifier	F - F	Room	1.5	2b	4	Added water has no effect
Emulphor A (19)	F	Room	.05-.5	2b	4	
2-Ethyl butyric acid (9)	F	100	.1	2a	1	
Ethylene glycol	D	Room	.5	2a	1	
2-Ethyl hexoic acid (9)	D - F	100	.2	3a	1	
Formol (35)	F	100	.2	2c	1	
Glycerol	D	Room	.05-.1	2b	4	F at conc'n .05 and .01%
Glyceryl monooleate (20)	F	Room	.7	2a	1	
Glyceryl monoricinoleate (20)	F	25	.5	2c	1	
Glycol bor-borate (20)	D	25	2.5	2c	1	
Glycol silicate (9)	F	Room	.02-.1	2b	4	
Gum Pontianack	F	25-100	.05	2c	1	
Hydro-resin (20)	F	100	.2	3a	1	
Isopon-T (19)	F	Room	.5	2a	1	Added water has no effect
Lead Aerosol OX (4)	F	Room	.2	2a	1	
Lead crotonate (38)	F	Room	.1	2b	4	
Lead stearate (27)	F - F	Rm.100	.005-.1	2a 2b 3a	1.4	Water increases foaming
Leothin (5)	F	100	.1	2a	1	
Soybean Lecithin (17)	F	Room	.1	2c	1	
Liourol wax	D - F	25-100	.1	2a	1	
Magnesium palmitate (24)	F - F	25	.1	2a 2b	1	
Martanol D (aqueous) (22)	D - F	25	2.5	2a 2b	1	
Methyl cyclotetrasiloxane	F	25	2.5	2a	1	
Methyl ricinoleate silicate (38)	F	100	.4	2a	5	
Morpel oil no. 501 (39)	D - F	Rm.100	1.5	2b 3a	1.4	
Morpelax B (39)	F	Room	1.5	2b	4	
Myristic acid (24)	F	25	.5	2c	1	
Nagconol F500 (29)	D	25	1.5	2c	1	
Nagconol N85 (29)	D	Room	.7	2a	1	
Naphthenic alcohols	F	Room	.5	2a	1	
alpha-Naphthol (16)	F	Room	.7	2a	1	
Nickel palmitate (38)	F	Room	.5	2a	1	
Nonethylene glycol monooleate (20)	F	25	.5	2c	1	
n-Nonyl alcohol (16)	F	100	.1	2a	1	
Oil-free phosphatides (B)	F	40	.5	2a	1	
Olive oil	F	Room	1.5	2b	1	
Ouricourol wax	D - F	24-100	.05-.5	2c	1	
alpha-Phenyl stearic acid (arade) (38)	F	25	2.5	2c	1	
Phosphorous (white) suspended in oil (38)	F	Room	.002-.05	2b	4	
Pine oil (43)	F	100	.4	3a	1	
iso-Propyl alcohol (34)	F	Room	.5	2b	4	
Propylene glycol diricinoleate (20)	F	Room	.7	2a	1	
Propylene glycol monooleate (20)	D	Room	.7	2a	1	
Pyrogallol	F	24-100	.05	2a	1	
Resin monomer G.R. 39 (12)	D	Room	1.5	2b	4	
Ricinoleyl sulfate (25)	F	Room	1.5	2a 2b 2c	1.4	F with water
Sheroscope "N" (26)	F	25	.5	2c	1	
Silver Palmitate (38)	F	25	.5	2a	1	
Sodium meta-silicate (30)	F	Room	.5	2a	1	
Span 20 (6)	F	Rm.100	.05-.5	2a 2b	1.4	Worse with water
Span 80 (6)	F	Room	.05-.2	2b	4	Added water has no effect
Span 85 (6)	F	Room	.05-.2	2b	4	Added water has no effect
Sulfatate (20)	D - F	Room	.5	2a	1	
Sulfuric acid	F	Room		2c	1	
Sulfurized sperm oil	F	Room	.5	2a	1	
Sulphonated tallow oil (23)	F	Room	1.5	2b	4	Added water has no effect
Supratol (22)	F	Room	.1	2b	4	Added water has no effect
Tannic acid (16)	F	25	.5	2c	1	Added water has no effect
Targol concentrates (35)	F	100-110	.5	2d	4	
Trichloroacetic acid	D - F	Room	.25	2a	1	
Tricetyl phosphate (10)	F	Room	.7	2a	1	
2,3,5-Trimethyl cresol	F	Room	.7	2a	1	
Triton (33)	F	Room	.5	2c	1	
Triton X (35)	F	25	.5	2c	1	
Tung oil	F	Room	.5	2b	4	
Tween 20 (6)	F - F	Room	.05-.2	2b	4	Added water has no effect
Tween 40 (6)	D - F	Room	.05-.2	2b	4	Added water has no effect
Tween 60 (6)	D - F	Room	.05-.2	2b	4	Added water has no effect
Tween 80 (6)	F - F	Room	.05-.5	2a 2b	1.4	Added water has no effect
Yelkin (5)	F	Room	.5	2a	1	
Yelkin 8D (5)	F	Room	.5	2a	1	
Yelkin 8SS (5)	F	Room	.5	2a	1	
Yelkin 8TS (5)	F	Room	.5	2a	1	

COMPOUNDED AGENTS

AGENTS	PROPORTIONS	GRADE	TEMP. RANGE	CONC'N %	TEST METHOD	OILS TESTED	REMARKS
Butyl carbitol	75%	E	Room	.4	2b	1	Anhydrous
Tergitol penetrant 4 wax	25%						
Butyl carbitol	89%	D	Room	.9	2b	1	Anhydrous
Tergitol penetrant 4 wax	11%						
Butyl cellosolve	50%	D	100	.8	3a	5	
Diethyl lauryl amido phosphate	50%						
Butyl cellosolve	75%	B - C	Room	.5	2b	1	B at butyl cellosolve conc'n .5%
Tergitol penetrant 4 wax	25%	A	Room	.5	2b	1	.07% water added
Caprylic acid	50%	E	100	.4	3ae	1	
Tergitol penetrant 4 wax	50%						
Diethylene glycol	3.0%	D	100-130	.4-1.	3d	4	Concentrate 9
Aerosol OT	3.5%						
Mujol	93.5%						
Diethylene glycol	2.6%	A	40-115	1.	3d	1	Concentrate 14
Calcium Aerosol OT	1.7%	A	100-170	3.	3d	4	
Mujol	95.7%	A	25-100	1.	3d	6	1% water added
		D - E	25-140	.25-1.	3d	6	
		C - E	125-180	.25-5.	3d	9	
Diethylene glycol	4.6%	A	70-140	.5	3d	1	Concentrate 15
Lead Aerosol OT	4.0%	A	110	2.-3.	3d	4	
Mujol	91.4%	C - E	30-140	.25-1.	3d	4	
		A - C	70-100	.5	3d	6	.5% water added
		A - C	70	.5	3d	6	Agent gradually deteriorates
		A - C	25-100	.5	3d	6	Agent gradually deteriorates
		A - E	100-140	.25-6.	3d	6	Agent gradually deteriorates
		A - E	100-140	.25-5.	3d	9	Agent gradually deteriorates
Diethylene glycol	80%	E	Room	.6	2b	4	
Penatrol 60	80%						
Diethylene glycol monooleate	5%	B	110	1.-5.	3d	4	Concentrate 2
Aerosol OT	2%	A	25-60	1.	3d	6	
Squibb's mineral oil	93%	A - E	60-130	1.-5.	3d	6,9	A at first. E on prolonged heating
Diethylene glycol	20%	E	Room	.6	2b	4	
Penatrol 60	80%						
Formamide	20%	E	Room	.6	2b	4	
Penatrol 60	80%						
Formamide	60%	E	Room	.2	2b	4	
Tergitol penetrant 4	60%						
Glycerol	67%	A	100	.6	3ae	1	
Aerosol OT	33%						
Glycerol	2%	A	70-100	.25	3d	1	Concentrate 19
Aerosol OT	2%	A	70-120	3.	3d	1	
Aeroshell 120 oil	92%	A	25-25	1.	3d	5	Reversible temp. cycle to 120°
		B	25-95	1.	3d	6	
		B	25-110	1.	3d	6	
		A - E	25-120	1.	3d	11	Agent deteriorates on temperature cycle to 120°
Glycerol	6%	A	25-120	.5	3d	1	Concentrate 21
Aerosol OT	2%						
Aeroshell 120 oil	92%						
Glycerol	4.8%	E	25-100	.5-2.	3d	4	Concentrate 3
Aerosol DGA	3.2%						
Mujol	92.0%						
Glycerol	5.0%	E	100-145	.25-2.	3d	4	Concentrate 18
Alkaterg 0	3.7%	F	100-145	3.	3d	4	
Mujol	91.3%						
Glycerol	4.8%	E	120-140	.25-1.	3d	4	Concentrate 5
Aluminum oleate	3.5%						
Mujol	92.0%						
Glycerol	4.1%	A	120-145	.5	3d	4	Concentrate 4. Reversible
Calcium Aerosol OT	4.3%	A	40-140	1.	3d	1	Temperature cycles for oils 1 & 4
Mujol	91.6%	B	25-140	.5	3d	1	A below 80°
		A	25-65	.25	3d	6	Agent gradually deteriorates at
		A	25-75	.5	3d	6	high temperature with oil A
		C - E	80-110	.25-1.	3d	6	
Glycerol	73.6%	A	100	.2	3a	1	B-10-186
Diethyl lauryl amido phosphate	26.4%	A	100	.06	3a	5	B at .03%, C at .01% conc'n
		F	100	.2	3a	6	
Glycerol	67%	A	100	.6	3a	5	
Diethyl lauryl amido phosphate	33%						
Glycerol	50%	C	100	.4	3ae	1	The detergent separated in bottle; only clear top layer used
Diethyl lauryl amido phosphate	50%						
Glycerol	33%	A	100	1.2	3a	5	
Butyl cellosolve	33%						
Diethyl lauryl amido phosphate	33%						
Glycerol	67%	F	100	.6	3a	5	
Dioctyl stearyl amine pyrophosphate	33%						
Glycerol	40%	D	100	1.	3a	5	
Butyl cellosolve	40%						
Dioctyl stearyl amine pyrophosphate	20%						

COMPOUNDED AGENTS

AGENTS	PROPORTIONS	GRADE	TEMP. RANGE	CONC'N %	TEST METHOD	OILS TESTED	REMARKS
Glycerol	2.4%	E	100-160	.25-.2	3d	4	Concentrate 17
Emulphor O	1.8%						
Nujol	95.8%						
Glycerol	70.4%	C	100	.2	3aa	50%10+70%	R-110-44
Lead Aerosol OT	29.6%	A	100	.03-.27	3aa	1	Less effective at conc'ns below .03%
		C	100	.2	3aa	9	
Glycerol	50%	A	Room	1.	2a	1	
Lead Aerosol OT	50%	A	100	.8	3aa	1	
		A - B	100	.8	3a	11	Became B after 20 min. bubbling
Glycerol	2.0%	E	100-180	.25-1.	3d	4	Concentrate 6
Lead stearate	1.2%						
Nujol	96.8%						
Glycerol	67%	D	100	.6	3a	5	F when butyl cellosolve added
Monolauryl dipolyglycol ortho-phosphate	33%						
Glycerol	67%	E	100	.6	2a	5	
2-Nitro 1-butanol	33%						
Glycerol	10%	B	40-140	.25-.2	3d	1	Concentrate 16
Octyl tripolyphosphate	10%	A	70-120	10.	3d	4	
Mineral oil	80%	A	25-80	.25	3d	6	
		A	25-100	.5	3d	6	
		A	25-140	1.	3d	6	
		C - E	100-140	1.-20.	3d	9	Agent rapidly deteriorates
Glycerol	50%	E	Room	.9	2b	4	
Penatrol 60	50%						
Glycerol	50%	E	Room	.2	2b	4	
Tergitol penetrant 4	50%						
Glycerol	98.5%	E	Room	1.5	2b	4	
Tergitol penetrant 4 wax	1.5%						
Glycerol	50%	B	100	.4	3aa	1	
Tetraoctyl pyrophosphate	50%						
Methyl cellosolve	80%	A	100	1.	3a	1	F after solvent boils away
Tergitol penetrant 4 wax	20%						
Oleic acid	50%	A	100	.2	3aa	1	
Tergitol penetrant 4 wax	50%	F	100	.2	3aa	25%6:75%	
Phenol	20%	E	Room	.6	2b	4	
Penatrol 60	80%						
Ridnoleyl sulfate	85.3%	E	26	1.5	2c	1	
Tergitol 68	14.7%						
Sapamine MS	5%	A	26-140	.25-.5	3d	1	Concentrate 1
Aerosol OT	2%	A	110	1.	3d	4	F when held at 150°
Squibb's mineral oil	93%	A	40	.25	3d	6	Less effective above 40°
		A	85	1.	3d	6	Agent deteriorates above 85°
		A	150	5.	3d	6	Agent deteriorates above 150°
		E	140	.25-.5	3d	6	
		A	90-130	2.	3d	9	Agent gradually deteriorates
Sapamine MS	4.0%	E	80-120	.25-1.	3d	1	Concentrate 15
Calcium Aerosol OT	3.7%	A	100-150	1.	3d	4	Not effective below 1%
Nujol	92.3%	D - F	50-140	.25-.4	3d	6	
Sapamine MS	4.3%	D	100-200	.3-1.	3d	4	Concentrate 7
Lead Aerosol OT	2.4%						
Nujol	93.3%						
Toluene	90%	E	Room	.7	2a	1	
Lead Aerosol OT	10%						
Toluene	50%	A	Room	1.4	2a	1	
Zinc Aerosol OT	50%						
Trisethanolamine	50%	E	100	.4	3aa	1	
Diethyl lauryl amido phosphate	50%						
Trisethanolamine	1.5%	C	100-135	.3	3d	4	Concentrate 10
Trisethanolamine oleate	3.5%	E	110-135	.5	3d	4	
Aerosol OT	3.7%						
Nujol	91.3%						
Trisethanolamine	1.6%	E	100-140	.5-.2	3d	4	Concentrate 12
Trisethanolamine oleate	4.2%						
Calcium Aerosol OT	5.8%						
Nujol	88.2%						
Trisethanolamine	1.8%	A	70-140	.5	3d	1	Concentrate 11
Trisethanolamine oleate	4.2%	A	100-160	2.	3d	4	Not effective below 2%
Lead Aerosol OT	5.1%	A	75	.25	3d	6	
Nujol	88.9%	B	75-100	.25-.5	3d	6	
		E	140	.5	3d	6	
		A	40-105	1.	3d	6	
		C	110-140	1.	3d	6	
		R	140	5.	3d	9	

Other observations.— When ethyl silicate or lead palmitate was present in the oil, it was observed by the method of aeration and evacuation (2b) that as the system was evacuated, the oil formed a stable foam until the bubbles grew to a certain size, whereupon the bubbles exploded like overinflated balloons, leaving a foam-free surface. With untreated oil, the bubbles stretch to such a size that it is not convenient to let them continue to expand to the bursting point in the equipment used. In methods involving evacuation, results would be contradictory depending on whether the pumping was stopped before the rupture point of the bubbles was reached (reporting C - E antifoaming), or the bubbles were exploded causing very rapid collapse (reporting A - B antifoaming). The phenomenon seems to be due to a predominantly elastic surface structure rather than a predominantly liquid one. Alternatively, the film becomes heterogeneous if stretched too far or too rapidly for uniformity of composition.

Another peculiarity is that phosphorated stearylamine (table XII) is a good defoamer for artificially oxidized Aeroshell 120 oil (8) after the oil has been filtered, but in the presence of the sediment the agent is without effect. This example is analogous to the greater ease of defoaming obtained when Moffett Field Used oil (9) is filtered to remove the sediment.

Steam emulsification.— An attempt was made to correlate the antifoaming properties of agents in lubricating oils with their effect upon the emulsification of water in the oil. Steam was blown for a prescribed time through 20 cubic centimeters of the oil containing the agent, in a cylinder immersed in a water bath at room temperature. The cylinder was then transferred to a water bath at 95° C, and the time in seconds for the emulsion to separate noted. (The procedure used was the Standard Method of Test for Steam Emulsion of Lubricating Oils, described in A.S.T.M. Standards, 1939, pt. III, pp. 132-135). Thirteen agents were tested, three of which were simple agents and ten compounded agents. All but five of those tested were excellent antifoamers (in the presence of water) both at room temperature and 100° C.

The correspondence between the steam emulsification numbers and the antifoaming grades was apparently random. A direct comparison of such unlike tests involves factors of such complexity that the results must be regarded as indecisive rather than definitely negative.

Summary

Aeronautical oils have been tested for foaming by several methods after the addition of hundreds of different materials and chemicals. The results are classified and tabulated in five tables.

Effects of concentration, of temperature, of the particular aeronautical oil used, and the presence of moisture as well as the mode of incorporation of the agent have been described and discussed.

Highly effective antifoaming agents have been found which are effective under almost all conditions. Special attention is directed to the mixtures of pure chemicals, such as an Aerosol with three to ten parts of glycerine.

APPENDIX V

KNOWN ADMIXTURES OF PURE CHEMICALS AS FOAM INHIBITORS

A practical solution to the problem of oil-foaming at elevated temperatures is strongly indicated by certain admixtures of pure chemicals, reported in table XIV of appendix IV. Those mixtures, present in concentrations as low as 0.02 percent, are responsible for the total inhibition of foaming of typical aeronautical oils up to temperatures of 150° C. The present appendix is concerned with the factors that have guided the choice of constituents in those mixtures and that will be of importance in compounding further agents for specified foaming problems. Commercial antifoaming materials used in such industries as paper or textiles are usually compounded mixtures.

A consideration of the large bulk of data collected on the subject of foam inhibition by chemical agents indicates that no single mechanism is capable of explaining all the observed cases. For example, Foulk and Miller (reference 3) have pointed out that the foaming of sodium sulphate solutions can be prevented by the addition of soap, although both are completely soluble and each by itself is a foamer. In many important cases of foam prevention the insolubility of the agent has been suggested as a prime requirement. This idea has been repeatedly expressed both in the printed literature and in restricted reports, although such cases as that exemplified by Foulk and Miller destroys its claim to generality. Many examples of soluble antifoaming agents are adduced in appendix VI. Still another mechanism of foam inhibition appears in the case where hydrochloric acid is added to soap solution: here the chemical reaction destroys the foaming agent. The foaming of milk can be reduced by the presence of water-soluble ethyl phosphate, which likewise indicates a different mechanism from that which is functioning when an insoluble liquid is used as a foam inhibitor.

The difficulties encountered in the search for properties that can be correlated either with foaming or defoaming ability has perhaps led to an undue emphasis on the many cases where insolubility of the agent has gone hand in hand with foam inhibition. It must be kept in mind that not only are there many cases of foam inhibition

by soluble agents but also that many emulsions of mutually insoluble liquids are known to be capable of forming foams of extraordinary stability (e.g., milk, crude petroleum).

Nevertheless chemical heterogeneity of the liquid film is in some cases an immediate cause of film collapse. The following statement by Fiske (reference 32) is not correct:

"It can readily be shown that foaming cannot be adequately prevented by an organic liquid which is completely dissolved. The presence of undissolved particles of the liquid must therefore be regarded as essential."

Nevertheless, the point of view expressed here was considered worthy of further attention, especially in view of the outstanding experimental success of certain oil-insoluble agents as foam inhibitors in oil solutions. The possible effectiveness of chemical inhomogeneity in the film in reducing its stability also has been encountered in the frequent correlation of insolubility and foam inhibition, as, for example, in the results reported in appendix VI.

If the foam-inhibiting agent is to form a heterogeneous liquid film, it is present in the body of the liquid as emulsion droplets. The factors promoting stability of the emulsion of the foam-inhibiting agent in the oil therefore would appear to be equally important in ensuring that the agent remain operative as a foam inhibitor. Stokes' law, while it leaves out of account the effect of a stabilizing agent on the interface, gives information concerning the hydrodynamic factors conducive to emulsions of at least temporary apparent stability.

$$V = (2/9) gR^2(\rho_2 - \rho_1)/\eta$$

where V is the velocity of settling of the emulsion particle, R is the radius of the spherical emulsion droplet, and the other terms have their usual significance. From this equation it follows that if the following requirements are met, the resulting emulsion will keep longer.

- (a) Small emulsion droplets
- (b) High viscosity of medium
- (c) Equal, or nearly equal, densities of the two phases.

The fourth, a chemical factor, more important than any of those yet mentioned, must be added, as it is the sine qua non of a stable emulsion:

- (d) Stabilizing agent at interface to keep emulsion droplets from coalescence or even from clumping when they collide.

It is only in the infrequent case that a single chemical agent has proved itself capable of acting effectively as a foam inhibitor throughout a range of temperature. This is not surprising, in view of the physical and chemical requirements that are to be met by agents capable of inhibiting foam formation. Any single insoluble agent to be suitable must possess the ability to sustain a stable emulsion of small-particle size in the oil medium and also act as its own stabilizing agent with respect to the external phase. In most cases, however, it has been found necessary to compound two or more agents before an effective foam inhibitor is produced. The purpose of the kind of mixture here envisaged is to supply:

1. An agent (A) to create heterogeneous films
2. A stabilizing agent (B) to keep A in suitable stable dispersion in the oil medium

Another requirement for stable emulsions can be attained practically by blending the compounded additive in a colloid mill. This reduces the particle size and renders the emulsion capable of being kept for a longer period before separation of the phases takes place, as well as frequently increasing the effectiveness of the foam inhibitory action.

Method

1. Search for suitable constituents.— The method of obtaining information about suitable constituents for compounded additives may be summed up in the phrase: "Use a foamer to catch a defoamer." Substances that stabilize emulsions are necessarily surface-active and as a result frequently act as foaming agents when present alone. The method described in appendix VI was found capable of extension with the needs of the present problem in mind. Substances known to be effective as stabilizing agents for emulsions were first dissolved in oil, forming a foaming system. This system was tested with other agents until a

suitable foam inhibitor was found. The foam inhibitor thus obtained is the agent A in the compounded additive, the agent B having already been dissolved in the oil. Using this method, a number of suitable agents were discovered and used as a basis for the manufacture of compounded additives. Much of the data already assembled in appendix VI is of use in this respect.

In table XIX of appendix VI information concerning foam inhibitors for oil solutions of known foamers is collected. In the cases where the inhibitor is given the grade A, the mixture foams less than the pure solvent oil; hence the mixture of inhibitor and known foamer is a good oil defoamer, even though each agent taken separately may be a foamer.

Supplementing the clues provided by this method, some further combinations of chemicals were selected by analogy, although not always with the same success.

2. Beaker bubbler method of testing foam inhibitory action.— It is not necessary to have an elaborate foam-measuring device for solutions that do not foam. A simple foam tester (not a foam meter) can be constructed using only a beaker and a sintered glass bubbler. Air is supplied at a rate suitable for the formation of foam, and passed through the bubbler. The oil in the beaker can be heated to any desired temperature for the purpose of the test, or the test can be conducted throughout a range of temperature. Any elevated temperature can be attained. The observation is made of how much foam can be formed by this means. Complete absence of foam is called Good; a quantity of foam less than that formed in the absence of the additive is called Fair. The terms "No effect" and "Stabilizer" are self evident.

Table XVI gives a list of compounded additives and their effect on the foaminess of NACA reference oil when tested by this method, at temperatures between 100° and 150° C.

The concentration of each agent in the final mixture tested is of the order of 0.01 to 0.05 percent. Full details of the concentration used and the temperatures at which the tests were conducted will be found in table XV of appendix IV.

Discussion

The lack of effect obtained in some cases does not detract from the validity of the theoretical argument. So little information is available concerning "oleophobic" agents and the type of surface-active agent required to keep them in stable dispersion in a medium of hydrocarbon oil, that many of the compounded additives here tried were themselves empirical, rather than based on a sure theoretical or pre-established footing. The results obtained furnish examples of substances that are a desirable constituent A and others that are suitable for constituent B.

Substances suitable as constituent A

Glycerol

Diethylene glycol

Triethanolamine

Substances suitable as constituent B

Sodium Aerosol OT

Calcium Aerosol OT

Lead Aerosol OT

Triethanolamine oleate

Several of the compounded additives, containing suitable combinations of A and B, have been tested in different oils, including a used oil and an oil known to be a persistent foamer. Their use in this connection has met with a fair degree of success. The results are tabulated fully in table XV of appendix IV.

The results of those tests show a very gratifying effect on the part of some mixtures. In general, the foam-inhibitory action is most marked on noncompounded oils (NACA reference oil, Aeroshell 120); greater difficulty is experienced when the oil is compounded (RPM Aviation) or has been heavily used; these require more of the anti-foaming agent. Many mixtures can be obtained that are

TABLE XVI.- LIST OF COMPOUNDED ADDITIVES AND THEIR EFFECT
ON NACA REFERENCE OIL AT 100° TO 150° C

Constituent A (Internal phase)	Constituent B (Emulsion stabilizer)	Effect on foam of NACA Reference Oil
Diethylene glycol mono-oleate	Sodium Aerosol OT	Fair
Glycerol	Sodium Aerosol DGA	No effect
Glycerol	Sodium Aerosol OT	Good
Glycerol	Calcium Aerosol OT	Good
Glycerol	Lead Aerosol OT	Good
Glycerol	Lead stearate	No effect
Glycerol	Aluminum oleate	No effect
Glycerol	Octyl pyrophosphate	Good
Glycerol	Emulphor O	No effect
Glycerol	Alkaterge O	No effect
Glycerol	Diethyl lauryl amido phosphate	Good
Sapamine MS	Calcium Aerosol OT	Good
Sapamine MS*	Sodium Aerosol OT**	Good
Sapamine MS	Lead Aerosol OT	No effect
Diethylene glycol	Sodium Aerosol OT	No effect
Diethylene glycol	Calcium Aerosol OT	Good
Diethylene glycol	Lead Aerosol OT	Good
Triethanolamine	Triethanolamine oleate plus sodium Aerosol OT	Fair
Triethanolamine	Triethanolamine oleate plus calcium Aerosol OT	No effect
Triethanolamine	Triethanolamine oleate plus lead Aerosol OT	Good
Oleic Acid	Tergitol Penetrant 4 wax	Good
7 ethyl, 2 methyl undecanol-4	Sodium Aerosol OT	No effect

*Formula = $C_{17}H_{33}CONHC_2H_4N(CH_3)(C_2H_5)_2(SO_4GH_3)$

**Formula = 2 ethyl hexanol sodium sulfosuccinate

completely effective on the noncompounded oils and have a strong foam-reducing effect on both compounded and used oils, at temperatures from room temperature to 150° C. It is only to be expected, however, that different additives introduced by the manufacturer or synthesized in the engine during use will have unpredictable effects on the foaming qualities of an oil and the effectiveness of any foam-inhibiting agent present in it.

Many of the mixtures tested are effective to temperatures as high as 150° C. In other cases the foam-inhibitory action disappears abruptly at a certain temperature and in a few cases; for example, diethylene glycol alone when finely subdivided, foam inhibition starts only at an elevated temperature. In general, a rise in temperature results in a foam of greatly reduced stability, but this is accompanied by a corresponding increase in ease of foam formation. In practice, the effect of this latter factor may even offset the advantage gained by the former one. In some cases the foam-inhibiting agent becomes inoperative above a certain temperature range and may even be permanently spoiled if heated above that range. The restraint on the foam stability being thus released while the ease of foam formation has been rendered so great at the elevated temperature results in the formation of a large volume of foam at a temperature that might be only 10° C above that where complete foam inhibition prevails. The temperature of the sudden foam appearance can be made to vary a little by using a different concentration of the foam inhibitor, and it is always at a lower temperature for used oil than for unused oil.

The hypothesis of foam inhibition, upon which is based the testing and compounding of the mixtures described in this appendix can be used to explain some facts previously observed as well as to make some general predictions concerning the nature of foam inhibitors. Some limitations of the hypothesis will be mentioned first.

Limitations of the hypothesis.— Not all compounded additives, where A and B are mixed, are effective as foam inhibitors. There are certain cases where other factors apparently come into operation to nullify the desired effect.

The hypothesis is limited to inhibition of foam and cannot be used to predict results concerning positive foaming action.

Previously observed facts explained by hypothesis.—

Substances that in some cases are foam stabilizers when present alone in the oil have been made foam inhibitors when water is present (see table XII, appendix IV); indeed, it has even been proposed that all foam inhibitors depend for their efficacy upon the presence of traces of water finely dispersed throughout the oil (reference 21), although appendix IV shows many examples of simple anti-foaming agents for dry oil. According to the present more general hypothesis, these systems are in themselves examples of compounded additives, in which water is constituent A and the chemical compound already added is constituent B. The inability of these systems to function at 100° C is readily explained by the loss of a necessary constituent, water. The first compounded agent operative at the latter temperature developed in the present investigation was attained by the substitution of glycerol for water in one of these mixtures. It is generally the case that the agent B in the aqueous as well as in the nonaqueous compounded additives is a surface active agent, capable of stabilizing an emulsion.

The action of 2-nitro 1-butanol is instructive. This substance is without effect unless finely dispersed either by a gear pump or much more especially by a colloid mill. Once dispersed as a fine emulsion it shows pronounced defoaming action at room temperature.

At 100° C this substance loses its ability to cause foam inhibition, presumably because it becomes more soluble at that temperature. On cooling, the foam-inhibitory action is recovered. Many other compounds listed in appendix IV have a parallel behavior as foam inhibitors and probably can be explained in the same way.

Corollaries of the hypothesis.— Some of the most effective foam inhibitors are oil-insoluble agents capable of sustaining stable emulsions in a hydrocarbon oil medium.

Foam inhibitors in a hydrocarbon oil system are not generally capable of inhibiting foam in all systems.

The presence of an emulsion-stabilizing agent is found to increase the effectiveness of those additives the action of which is otherwise only temporary.

Summary

1. Chemical inhomogeneity in the film has been suggested as one very effective mechanism of film instability and hence, of foam inhibition. Experimental evidence is given in its support.

2. A series of mixtures is compiled in accordance with this hypothesis and results given of their effect as foam inhibitors in hydrocarbon oils.

3. A practical solution of the problem of oil foaming is indicated by the use of some of the compounded agents here reported, such as an Aerosol OT plus glycerol.

APPENDIX VI

THE INHIBITION OF FOAMING IN A SERIES OF SOLVENTS
CONTAINING KNOWN FOAMERS

The present appendix reports a series of experiments to determine the effect of incorporating various known agents in different well-defined systems capable of forming foam. The object of the investigation is to uncover some operative factors in the inhibition of foaming by means of antifoaming agents. Two types of solvent were selected: the first a series of water-miscible liquids and the other a white mineral oil. The results are reported in two separate sections of this appendix. The work on the oil solutions is of especial significance because of its applications in the admixture of foam inhibitors for aeronautical lubricating oils. (See appendix V.)

I. FOAM-FORMING SYSTEMS WITH WATER-MISCIBLE SOLVENTS

The liquids used were not specially purified. They are, nevertheless, incapable of forming bubbles of stability greater than about half a second upon exposure to the atmosphere until a known foaming agent is added. The non-aqueous solvents used are triethanolamine (Eastman Kodak) Diethylene Glycol (Eastman Kodak). These were chosen because of their low vapor pressure. Various solutes were then tried in two liquids with the primary purpose of determining if a foaming system would be obtained. The results offer marked contrast with the effects of the same solutes in water. In table XVII are collected data on the foaminess and solubility of the solutes in two of the non-aqueous solvents. The capacity for forming a foam was tested by shaking the solution in a test tube, and preliminary tests were conducted at about 70° and at 100° C. The higher temperatures were first chosen because at room temperature the solutions were generally too viscous to form a foam by shaking. Room-temperature tests then were made by bubbling air through the solution, dispersing the gas by means of a sintered glass disk. The solutions exhibited similar behavior, alike at room temperature, at 70° and at 100° C. A difference in the amount of foam formed at different temperatures was observed frequently but could be traced to a difference in the solubility or the viscosity.

TABLE XVII.- FOAM BEHAVIOR OF SOME SOLUTES
IN TRIETHANOLAMINE AND DIETHYLENE GLYCOL

<u>Solute</u>	<u>Solubility</u>	<u>Comments</u> ¹
<u>a. Triethanolamine</u>		
Aerosol OT	soluble	Foam
Triethanolamine oleate	soluble	Foam
Aluminum oleate	soluble hot	Foam hot or cold
Soybean lecithin	soluble	Foam
Sodium stearate	soluble hot	Foams
Benzene plus chloroform	soluble	Clear solution; foams
Diethylene glycol	soluble	No foam
Benzene	insoluble	No foam. Chro- matic emulsion
Cerotic acid	soluble hot	No foam hot or cold
Saponin	soluble hot	No foam hot or cold
Cholesterol	soluble hot	(2)
<u>b. Diethylene Glycol</u>		
Aerosol OT	soluble	Foam
Benzene	soluble	Foam
Aluminum oleate	insoluble	Slight foam
Sodium pamitate	soluble hot	Slight foam hot
Sodium stearate	soluble hot	Slight foam hot
Calcium palmitate	soluble hot	No foam hot
Aerosol 1B	soluble	No foam in ab- sence of water
Butyric acid	soluble	No foam
Oleic acid	soluble	No foam
Saponin	soluble	No foam
Cholesterol	soluble hot	(2)

¹Foam - solution markedly foamy.
Slight foam - only a few bubbles capable of forming.

²Turbid solution foams to 148° C; clear solution above 148° C foams slightly; 148° C is the melting point of cholesterol.

Differences between the nonaqueous foaming systems and aqueous systems are both physical and chemical in character. The chief physical differences are the viscosity and the rate of viscosity change with temperature. Everything else being equal, a decrease in viscosity will be accompanied by a decrease in foam stability, as has been shown by Bartsch (reference 33). This has been demonstrated for hydrocarbon oils in appendix III. The parallel variation of foam stability and viscosity with temperature probably is due to the reduction of intermolecular forces which result in a simultaneous loosening of the cybotactic structure both in the bulk liquid and at the liquid-air interface. (Cf. references 6, 11, and 35.) While a decrease in viscosity leads to a decreased foam stability by facilitating drainage, it is nevertheless conducive to greater ease of foam formation upon shaking or beating: it is this latter effect that is responsible for troublesome foaming in industrial processes at higher temperatures. Ease of foam formation has an inverse relation to viscosity or, if the viscosity is constant, may depend on some factor as the amount of gas available - for example, degree of carbonation of beer (reference 36) aeration, and so forth, and is not related to foam stability.

The behavior of certain solutes in the nonaqueous solvents is in marked contrast to their behavior in aqueous medium. Solubilities of organic compounds are, in general, greatly enhanced in nonaqueous solvents. Foaming ability is very different, as illustrated, for example, in the failure of saponin or Aerosol 1B to form any foam in the absence of water.

Effect of Some Chemical Additives on Some Well-Defined Foaming Systems

A selection of five foaming systems, three nonaqueous and two aqueous, and of 22 chemical agents was made. The foaming systems were the following:

- I. 7.74 percent Aerosol OT in Triethanolamine
- II. 5.55 percent Aerosol OT in Diethylene Glycol
- III. 34 percent Triethanolamine Oleate in Triethanolamine
- IV. 1.55 percent Nacconol NR in water
- V. 0.85 percent Aerosol OT in water

The chemical agents used are listed in table XVIII.

Further series of tests were made later on oil solutions of sodium Aerosol OT (see pt. II). The ability to form foam was first tested at 100° C by a shaking method, similar to that employed by Wilson and Ries (reference 9). Thereupon the agent was incorporated to the extent of 1 percent of the volume of the original solution. This is a relatively high concentration for an antifoam. The results in every case could be classified in three easily distinguished groups: (a) complete inability to form foams, marked "A" in table XVIII, (b) marked loss of the ability to form foam, marked "C" in table XVIII, and (c) no observable effect on the ability to form foam, marked "E" in table XVIII.

The other columns of table XVIII record the solubility of the additive and the effect of the additive when added to a single film of the liquid system. This latter "pop" test has been developed by Dr. J. V. Robinson in this laboratory. (See appendix II.) A film of the foaming liquid is formed on a loop of platinum wire and another platinum wire, previously dipped in the additive under test, is gently touched to the thick part of the liquid film. Immediate breaking of the film by the additive is marked "A" a delayed rupture but still definitely due to the influence of the additive is marked "C" and no effect on the stability of the film is marked "E."

Discussion of Results

The behavior of different foaming systems with respect to additives are compared according to the following plan:

- (a) Aerosol OT in triethanolamine and in diethylene glycol compared with Aerosol OT in water
- (b) Aerosol OT in water compared with Nacconol NR in water
- (c) Aerosol OT in triethanolamine compared with triethanolamine oleate in triethanolamine.

Comparisons are made of the first column in each system, between inhibiting effect (A or C) and no effect

(E) on the foaming capacity of the system. Thus A and C are counted as an agreement, but C and E count as a disagreement. On this basis an examination of table XVIII reveals that more similarities or regularities are to be found than differences. The different agents exhibit completely parallel behavior (0 percent deviation) in the non-aqueous solutions of Aerosol OT. The deviation of behavior between the nonaqueous solution and the aqueous solution of Aerosol OT is 8 in 22 or 36 percent, that between the two different solutes in triethanolamine is 7 in 22 or 32 percent. The behavior of additives on foaming systems thus is seen to bear a certain degree of relationship, in contradiction to the preliminary impression, based on less widely distributed data, that the defoaming action of an additive is highly specific. The comparison of these water-miscible foaming systems with respect to the anti-foaming properties of additives indicates that a chemical similarity in either the solute or the solvent of the systems will lead to about a 75 percent similarity in the effects of additives, while a more complete resemblance of the systems may result in a 100 percent correspondence.

Of the 22 agents tried, in the concentrations reported, only four are effective foam inhibitors for all five foaming systems. The remainder of them are variously effective on from zero to four out of the five systems. The action of organic phosphates appears to be especially pronounced.

In a majority of the cases studied an optimum concentration exists for defoaming action, even though this optimum amount sometimes lies definitely above the solubility of the agent. When this concentration or amount is exceeded, the foaming ability of the mixture frequently reasserts itself. This is true, for example, in the cases of additives 8, 9, and 12 and 18 when added to the non-aqueous solutions of Aerosol OT. The arbitrary choice of a concentration of 1 percent in table XVIII does not always permit the true character of a defoaming agent to be properly represented. In higher concentrations some of the agents reverse the effect that they exercise at a concentration of 1 percent. Such examples are noted in table XVIII.

The marked effect caused by the presence of even minute amounts of water has been noted in some of the studies of the foaming of oil. In the present investigation it was found that, after defoaming action had been

TABLE XVIII (Continued)

Agent	Aerosol OT in tri- ethanol- amine			Triethanol- amine oleate in triethanol- amine			Nacconal NR in water at 24° C			Aerosol OT in di- ethylene glycol			Aerosol OT in water		
	I			II			III			IV			V		
	i	ii	iii	i	ii	iii	i	ii	iii	i	ii	iii	i	ii	iii
11. 2-amino 2-ethyl 1,3-propanediol	E	s	C	E	s	C	E	s	C	E	s	E	E	s	C
12. Sapamine MS	A	i	A	E	s	E	E	i	E	A ⁴	i	A	C	i	E
13. B.O. 1	C	i	A	A	i	A	E	i	C	C	i	A	C	i	C
14. B.O. 2	C	i	A	A	i	A	E	i	C	C	i	A	C	i	C
15. Penatrol 60	C	i	A	E	s	A	E	i	E	C	i	A	C	s	C
16. Diethylene glycol	E	s	E	E	s	E	E	s	C	E	s	E	C	s	C
17. Ethyl phosphate	C	s	A	C	s	A	C ¹	s	E	C	s	A	C	s	C
18. Tween 80	A	i	A	E	s	E	E	s	E	A	i	A	E	s	C
19. n-nonyl alcohol	C	s	A	C	s	A	A	i	A	C	s	A	C	i	C
20. Hydroquinone	E	s	E	E	s	E	E	s	E	E	s	E	E	s	E
21. Phenol	E	s	E	E	s	E	C	s	C	E	s	E	E	s	E
22. n-butyl phthalate	A	i	A	C	s	A	E	i	C	A	i	A	E	i	C

¹A in higher concentrations than the 1 percent here referred to.

²E in greater amounts, even though 1 percent was incompletely soluble and was a class A defoamer.

³A in greater amounts when the solubility is exceeded, although 1 percent was soluble and was without effect (E).

⁴E in concentrations above and below 3 percent; the only example of any concentration other than 1 percent cited in the table; compare footnotes 2 and 3.

achieved, addition of small amounts of water to the non-aqueous systems did not generally affect the result. This was true even in some cases where the solubility was very greatly altered by the presence of the water. When the best defoamers were used the solution could be diluted with water to three or four times its original volume before foaminess would begin to reappear.

Theory of Foam Inhibition

(i) Correlation with solubility of additive.— Some writers have stated that a defoaming agent should be, or must be, insoluble in the foaming system to which it is added. Table XIX expresses the results of the present study.

TABLE XIX.— CORRELATION OF THE EFFECT OF AN ADDITIVE
WITH SOLUBILITY

Effect of additive	Number of insoluble additives	Number of soluble additives
A	23	6
C	18	16
E	<u>13</u>	<u>34</u>
Total	54	56

This table shows that the most pronounced foam inhibitors are preponderantly insoluble, those that exhibit a partial defoaming action may or may not be insoluble, and a majority (60 percent) of the soluble additives are without effect. It is of interest, however, to observe that an additive need not be insoluble to be an effective foam inhibitor, or an effective foam breaker.

(ii) Correlation with film-breaking "pop test" of appendix II.— Some of the mechanisms of defoaming action are best observed when a drop of the additive is placed directly on a film of the foaming system. In some cases the

film snaps or "pops" immediately (A), in other cases the reaction is more delayed (C) or possibly does not occur at all (E). This test can therefore be used to make a classification of the additives into three groups. The correlation of this classification with the foaming tests in bulk is given in table XX, condensed from table XVIII.

TABLE XX.— CORRELATION OF THE EFFECT OF AN ADDITIVE
FILM-BREAKING TEST

Effect of additive in bulk test	Number and effect of additives in film-breaking test		
	<u>A</u>	<u>C</u>	<u>E</u>
A	26	3	0
C	18	12	4
E	2	15	30

It can be seen from table XX that an immediate rupture of the film on addition of the additive generally denotes an excellent defoaming agent, but that when no effect on the film is obtained the additive, though probably without effect, may yet exercise a partial defoaming action but never, in any example yet met, complete defoaming action. The degree of correlation at the extreme (A to A and E to E) is the most pronounced.

In those cases where addition of the additive does not result in immediate rupture, those additives that are without effect on the film stability will, if they are soluble, diffuse into the body of the film without visual effect on the surface; if insoluble they are left as either a solid or as a liquid lens on the surface. When rupture of the film is due to the additive but is so delayed that the surface can be watched, three different mechanisms can be observed: (a) when a drop of additive is added to the center of the film, the solution slowly draws back from that spot, getting thinner in the center and thicker at the edges until the central portion snaps. (b) On a thick liquid film the additive is without effect, sitting

as a separate drop on top of the liquid without spreading. On a thin film it spreads out rapidly and breaks the film. (c) In aqueous systems in particular, where evaporation plays a part in maintaining a thin film in the presence of a thick film (reference 16), the spreading on the thin film was not visible but the film ruptured immediately when its thinnest part came in contact with the additive.

Those differences in visible effect may be due respectively, to slow spreading on a thick film, slow spreading on a thin film and rapid spreading on a thin film. There are two hypotheses to account for the instability of a liquid film when an additive is spread on the surface. Hardy (reference 18) regards differences in concentration at the two liquid-air interfaces as exercising an unsymmetrical restraint on the liquid between and causing an ultimate collapse. "When the interfaces are not similar it is like an unannealed plate." Neville and Hazlehurst (reference 20) state that a film can persist only so long as evaporation and its resulting temperature gradient provide a flow of liquid into the thin portion to counteract drainage; an effect opposite to those discussed by Gibbs (reference 34) as examples of the tendency of the interior of the film to flow downward. An additive, by lowering surface tension, might decrease the flow of liquid into the thin film and cause a rupture at that point.

A delayed film-rupture test as described in (b) in the foregoing is shown by n-butyl phthalate added to Nacconol NR solution and by "Carbitol" maleate added to the solution of triethanolamine oleate in triethanolamine. Bulk surface tensions and interfacial tensions were measured on those two systems, using the DeNuoy tensiometer. The data obtained are listed in table XXI.

TABLE XXI.— SURFACE AND INTERFACIAL TENSIONS BY DENOY

TENSIOMETER

Liquid	(Temp.)	(Surface Tension in dynes/cm)	(Interfacial tension in dynes/cm)
(a) n-butyl phthalate	27° C	35.6	1.5
(b) 1.5 percent Nacconol NR in water	27° C	31.5	
(a) "Carbitol" maleate	25° C	40.1	2
(b) 34 percent triethanolamine oleate in triethanolamine	25° C	36.5	

The spreading coefficient for a liquid a to spread upon another liquid b is given by Harkins (reference 35) after Dupre.

$$S = \gamma_b - (\gamma_a + \gamma_{ab})$$

From this equation it can be seen that under normal circumstances Nacconol NR dissolved in water (1.55 percent) will spread on n-butyl phthalate, and triethanolamine oleate dissolved in triethanolamine will spread on carbitol maleate. Observations of those two effects, using powdered talc on the surface of the lower liquid, confirmed the prediction. It has already been stated that the lower liquid, in each case, does not spread on a thick film or on bulk volume of the other liquid, and this too is in conformity with the spreading coefficient: a spreads on b but b does not spread on a. However, since liquid a does in each case spread on a thin film of liquid b, the value of γ_b for a thin film appears to be greater than γ_b for a thick film or bulk volume. From the equation above, γ_b for a thin film of Nacconol NR solution must be greater than 37.1 dynes and γ_b for a thin film of triethanolamine oleate solution in triethanolamine must be greater than 42.1 dynes. In both cases this represents an apparent increase in surface energy of the thin film by more than 6-7 dynes per centimeter. The two liquids in each pair have nearly the same surface tension and a low interfacial tension; in both cases the increase in surface tension of the thin film is just sufficient to overcome the (small) difference between the two surface tensions added to the low interfacial tension. It is therefore to be expected that the phenomenon of delayed rupture as described for the foregoing two cases would only be apparent in those examples where the two liquids meet the specified conditions.

(iii) Mechanisms of foam inhibition.— The results of the present investigation indicate that the chemical inhibition of foaming may be accomplished by more than a single mechanism. In some cases additives capable of breaking single films are yet not effective in inhibiting foaming of a liquid when present in bulk and there are also different ways in which an additive is capable of destroying a film. In more complex cases it is to be expected that several factors are simultaneously operative. No single

known theory of mechanism can be applied to all possible examples. In the present instance the added foaming agent may well also act as a dispersing agent for the foam inhibitor and so enhance its effect.

II. FOAM FORMING SYSTEMS WITH WHITE MINERAL OIL

Squibbs mineral oil selected for this study exhibits kinematic viscosity 360 Saybolt seconds at 100° F. The variation of L_f with temperature was obtained using a sintered glass bubbler (method 3b, appendix II). Lead Aerosol OT and a lecithin (Yelkin BD), two agents of widely different character and known to enhance the foaminess of the original oil, were added and L_f values at different temperatures obtained by the same method. The results are reported in table XXII. At the higher temperatures the increase in foaminess of the original oil due to the foaming agents is always considerably less marked, and has completely disappeared in the case of the lecithin at 100° C. Consequently the effect of foam inhibitors was tested at room temperature in those cases.

TABLE XXII.— INFLUENCE OF YELKIN BD AND LEAD AEROSOL OT ON THE FOAMING ABILITY OF SQUIBB MINERAL OIL

Temperature °C	Pure mineral oil	Mineral oil 0.3 percent Yelkin BD	Mineral oil 0.5 percent Lead Aerosol OT
22	($L_f = 6.8$ min.)	($L_f = 88$ min.)	—
46	2.2	—	($L_f = 11$ min.)
56	1.3	4.6	7.6
64.5	.9	2.3	4.3
78	.5	1.2	1.9
100	.2	ca. .2	.6

The method of testing the effect of chemical agents on the foaming of oil solutions of lecithin and lead Aerosol OT was by beating and evacuation (Method 2a, appendix II). In each case approximately 0.5 percent of the agent is added and incorporated by stirring mechanically. The results for 11 agents are given in table XXIII with, for comparison, the effect of the agent on aeronautical lubricating oil without additive (Aeroshell 120).

There is no complete correspondence in the results for the 3 liquids: 3 of the 11 agents exhibit the same effect on 2 out of the 3 liquids. This is about the degree of correspondence found in part I.

TABLE XXIII.— EFFECT OF VARIOUS AGENTS ON THE
FOAM INHIBITION OF SOME OIL SYSTEMS
(Room temperature)

Agent	Pure Aeroshell 120	Mineral oil 0.3 percent Yelkin BD	Mineral oil 0.5 percent Lead Aero- sol OT
Ethyl oleyl glycol o-phosphate	A	E	A
Trioctyl tripolyglycol tetrapolyphosphate	E	E	A
Tetraoctyl pyrophos- phate	A	E	C
BO-1	A	A	A
Ethyl phosphate	A	C	A
Diethyl laurylamido phosphate	A	A	E
Phosphorated stearyl- amine	A	A	A
Zinc Aerosol OT	A	E	C
Alronol 90	A	A	A
Sorbitol dilaurate	A	E	A
Glycerol	E	—	A

A, excellent foam inhibition
C, moderate foam inhibition
E, no effect

Tests at 100° C by the test-tube shaking method (Method 1d) are conducted on a 2 percent solution of sodium Aerosol OT in Squibb mineral oil, for direct comparison with table XVIII of part I. Concentrations were tested at intervals of 1 percent and are listed in the second column of table XXIV.

TABLE XXIV.— EFFECT OF VARIOUS ADDITIVES ON THE FOAM
INHIBITION OF 2 PERCENT SODIUM AEROSOL OT
IN MINERAL OIL AT 100° C

	(percent)		
Ethyl oleyl glycol o-phosphate	1 and higher	Insoluble	E
Trioctyl tripolyglycol tetrapolyphosphate	1 to 10	Soluble to 6 percent	E
2-amino-2-methyl-1-propanol	1 to 3	Soluble	E
Tetraoctyl pyrophosphate	1	Insoluble	E
Diethanolamino ethyl phosphatidic acid	1 to 2	Soluble	E
Mono-oleyl dipolyglycol o-phosphate	1 to 2	Soluble	E
Diethylene glycol mono-oleate	1 to 5	Insoluble	A (opt. 4 percent)
2-amino-2-ethyl-1, 3 propanediol	1 to 5	Soluble	E
Sapamine MS	1	Insoluble	A
BO-2	1 to 20	Insoluble	A (opt. 2 percent)
Ethyl phosphate	5	Insoluble to 85 percent	A to 85
Phenol	1	Soluble	E
Penatrol 65	1 to 2	Insoluble	E
2-nitro 1-butanol	1 to 10	Insoluble	C (opt. 5 percent)
Propylene glycol diricinoleate	1 to 3	Soluble	D (opt. 2 percent)
Pyrophosphatidic acid	1 to 5	Soluble	E

TABLE XXIV (Continued)

	(percent)		
Ethyl alcohol	1	Insoluble	A (below b.p.)
Propylene glycol mono- laurate	1 to 4	Soluble	E
Nona-ethylene glycol mono- laurate	1 to 3	Soluble	E
Glyceryl mono-oleate	1 to 4	Soluble	E
Octyl alcohol	1 to 10	Soluble	E
Glycerol	1 to 15	Insoluble	A (opt. 2 percent)
Triethanolamine oleate	1 to 6	Insoluble	A at 3 percent E at 6 percent
Triethanolamine	1 to 4	Insoluble	E at 3 percent C at 4 percent
5 percent aluminum palmi- tate in pine oil	1 to 10	Insoluble	E

Of the agents listed in table XVIII only 3 are inhibitors for the oil solution. Many other additives, effective in the water-miscible solvents, were not effective in the oil solution of the same foaming agent. Consequently no correlation or regularity could be established between the two types of solvent.

The importance of these studies on oil systems lies chiefly in their application to the selection of compound foam inhibitors for lubricating oils. In table XXIII, for example, it is found that glycerol is without effect on the foaminess of pure Aeroshell 120 but completely inhibits the foam formation of a lead Aerosol OT solution in oil. In effect, the mixture of lead Aerosol OT and glycerol has reduced the foaminess of the system to a point far below even that of the untreated oil. Similarly in table XXIII the mixtures

1. Glycerol plus sodium Aerosol OT
 2. Sapamine MS plus sodium Aerosol OT, and
 3. Diethylene glycol mono-oleate plus sodium Aerosol OT
- are suitable compounded agents for the foam inhibition of oil.

In appendix V the effect on foam characteristics of aircraft lubricating oils of mixtures suggested by tables XXIII and XXIV, as well as some others, are reported and discussed.

Summary

Pure liquids do not foam. Foaming is due to added foaming agent. Such well-known antifoams as ethyl ether and amyl alcohol operate only when directly applied to foam and are usually inactive when dissolved in the liquid. All of the agents here studied were first dissolved or dispersed in the liquids and some were nevertheless highly effective as antifoamers.

A number of agents have been tested as chemical defoaming agents for several systems, aqueous and nonaqueous, containing known added foamers. When such foaming systems are compared with respect to the antifoaming properties of additives, a chemical similarity in either the solute or the solvent of the systems leads to about a 75 percent similarity in the effects of the additives, while a closer resemblance may lead to a 100 percent correspondence, as for example, between Aerosol OT in triethanolamine and in diethylene glycol. If dissimilarity is pronounced, no correlation or regularity can be found.

The most complete defoamers are usually but not always insoluble. In some cases excess of an "insoluble" antifoam nullifies its effect, hence, in these cases there is an optimum amount where solubility is slightly exceeded. Results of bulk foaming tests are shown to bear a large degree of correspondence with the action of an additive on a single film. The spreading of additives on single films is discussed from the point of view of surface tensions. The surface tension of a thin film of liquid appears to be 6 to 7 dynes per centimeter greater than that of the bulk liquid. More than one mechanism must be postulated to account fully for all types of foam inhibition by chemicals.

Studies of the effects of chemical agents on the foam characteristics of mineral oil solutions of known foamers are described and shown to be of value in obtaining suitable foam inhibitors for aircraft lubricating oils.

APPENDIX VII

ATTEMPTS TO REMOVE FOAMING AGENTS FROM LUBRICATING OIL

Since lubricating oil is primarily a complex mixture of hydrocarbons, it is believed that the separation of some nonhydrocarbon constituent, either dissolved or dispersed, from the oil should eliminate or greatly diminish foaming.

Five methods have been used in the attempt:

- A. Segregation of the constituent in the foam or "frothing off"
- B. Adsorption on an active surface
- C. Chilling
- D. Solvent extraction
- E. Segregation in an oil-water interface, similar to the method of frothing off

A. Froth Segregation.— Segregation of the solute in aqueous solutions by frothing has been reported repeatedly in the literature, and many quantitative experiments of this kind have been published by McBain and his collaborators. Both positive and negative adsorption have been measured. This is the first time segregation by frothing has been attempted in a nonaqueous system such as lubricating oil.

The method involves the comparison of the oil obtained from collapsed foam with the residual oil and with unfoamed oil. The foam is produced continuously by bubbling gas through a column of oil, the column being sufficiently long to allow good drainage of liquid from the foam films. The drained foam is collected in a separate vessel just before collapse. (See fig. 12.) The gas used to produce the foam (air or nitrogen) was introduced through a submerged jet at such a rate (0.5 to 1.0 liter per hr) as to produce a continuous stream of small bubbles.

This method was applied to Aeroshell 120. The receivers were changed at irregular intervals—that is, when fractions

of from 10 to 60 milliliters of oil from the collapsed foam had been collected. It was found that when the gas was passed rapidly through the oil, producing a stream of coarse bubbles, the froth column was continually broken, and only small quantities of oil were carried into the receiver. When the gas stream was slow, giving fine bubbles, the foam produced was relatively stable, and the receiver was filled steadily at a rate of approximately 3 milliliters per hour.

The fractions in the receiver were analyzed for change in composition with a Zeiss interferometer, reading refractive indices to six significant figures, using a 0.5 centimeter cell. The frothed-off samples were compared with either the residual oil in the tube or with the original oil.

Using dried air or nitrogen, the frothed-off samples were identical with the original oil within the experimental error. Water dissolved in the oil from wet air lowers the refractive index appreciably. A sample of residual oil which had been frothed off for several hours had the same foaming tendency as the original Aeroshell 120 oil when tested by aeration-evacuation technique.

With RPM Aviation oil, which ordinarily produces a copious, stable foam, a positive result was obtained. The additive was removed in the froth to such an extent that the residue resembled ordinary aeronautical oil. With NACA reference oil a large difference (27 interferometer units) in refractive index between the frothed off samples and the original oil was found, but foaming tests have not been completed on the various portions.

B. Adsorption Experiments.— Attempts to adsorb the foaming constituent of Aeroshell 120 on Norit (charcoal), Darco (charcoal), and diatomaceous earth were unsuccessful. Using a charcoal activated by heating to dull red heat under vacuum, Aeroshell 120 was altered in refractive index to an extent corresponding to 96 units of the interferometer, using 0.5-centimeter cells. This experiment is still in progress; so the significance of this single positive result is yet to be evaluated.

C. Chilling.— It was found that chilling of certain aeronautical oils to a temperature of 0° C or below results in a very marked, though temporary, reduction of the foaming

capacity of the cooled oil after restoring it to room temperature. This effect is maintained not only while the oil remains cool, but even after as much as 48 hours at room temperature. However, after two or three days at room temperature the oil foam regains its original stability. The chilling effect may also be undone simply by warming the oil to 50° C or 60° C. It is completely reversible. The chilling effect has been observed with NACA reference oil, Aeroshell, RPM Aviation and Standard Aviation but does not appear with Gulf Airline or with medicinal mineral oil. It is obtained with used as well as with new oil.

Samples of chilled and unchilled oils (NACA and Standard Aviation) were compared in the Beckman-Photoelectric Spectrophotometer, all the samples being at room temperature at the time of testing. The results indicate that the samples are distinctly different after having been chilled. At 5600 Å wave length, the chilled Standard Aviation sample transmitted only 92.5 percent as much light as the corresponding unchilled sample. At 4400 Å wave length the chilled oil transmits more light. The percent transmission-wave length curves are difficult to interpret further from present information.

The chilling effect is analogous to a result obtained at higher temperature with the phenol extract of an oil. When this extract is added to the oil, it tends to stabilize foam formed at 100° C. However, after the oil cooled down to about 15° to 18° C, the foamability was reduced to its original value. When the oil is rapidly heated to 100° C, there is a time lag in the restoration of the foam stability. This is the same behavior as shown by a chilled oil on heating, with an upward shift in temperature scale.

The results of the chilling experiments may be explained by the effect of temperature on the solubility of the foaming agent, which is in solution at normal temperatures and is precipitated when the oil is cooled. The foaming would be reduced as long as this substance remains out of solution. It might be sorbed by wax coming out of solution. If it goes back into solution only very slowly at room temperature the nonfoaming character of the oil would be retained at first. Slight heating would hasten the solution of such a substance and thus cause the original foaminess to be restored. This reasoning is supported by the fact that the highly colored oils exhibit this chilling effect whereas the clear oils (Gulf and Mineral Oil) do not, although

neither microscopic nor ultramicroscopic examination revealed the presence of a precipitate.

Several experiments were performed in the attempt to filter, extract, or adsorb the chilled-out constituent. In all cases, the oil was first chilled, then subjected to the separation process, and finally tested to determine whether the antifoaming effect was temporary or permanent.

Filtration was carried out with ordinary coarse-grain filter paper in a Buchner funnel. A second method consisted of mixing the oil with infusorial earth (either before or after chilling) followed by filtration, the infusorial earth serving both as a possible adsorbing surface and as a filter aid. A sample of extremely finely divided (pyrophoric) iron was also used for this purpose. Most of these experiments were done on NACA reference and RPM Aviation oils (120 grade).

In only one instance was there direct evidence of the removal of a foaming agent. It was found that the foaming tendency of RPM Aviation oil was reduced permanently after chilling and filtration, using infusorial earth as a filter-aid. The heated oil now foamed only as little as Aeroshell 120 both at room temperature and at 100° C. The temporary chilling effect previously observed is more pronounced than this permanent effect.

The second line of approach was to attempt an extraction of the chilled-out agent with the use of various solvents. The solvents employed were water (cold and hot), 0.5 normal sodium hydroxide solution, 0.1 normal hydrochloric acid solution, furfural, phenol, cresol, and aniline. The extractions, with one exception, had no effect on the foaming characteristics of the oils used; the furfural extracted oil had a slightly lowered foamability.

It was observed that after removing the oil from the box containing dry ice, there appeared on the surface of the solidified oil a number of white crystals, which grew in size and number as the oil became warmer. They were distinct from the water which had condensed on the surface. That these crystals were not ice was indicated by the fact that they remained even after the temperature of the oil rose above 0° C. Furthermore, as the temperature of the oil approached that of the room, the crystals changed to a fine suspension of white, waxy particles. When the oil was chilled in a crystallizing dish, these particles could be easily removed with a spatula, most readily just before

the pour-point of the oil was reached. The separated mixture consisted of a heavy suspension of white particles in oil, which remained undissolved in the oil for several weeks.

A sample of NACA reference oil was chilled and the precipitate on the surface removed with a spatula. This procedure was repeated five times and then the residual oil subjected to a foaming test. Although this oil foamed less than the original, the effect was not nearly as marked as with the chilled oil which was not skimmed. As before, the normal foaming capacity returned after heating the oil.

The results of the chilling experiments may be summarized as follows:

- (1) Chilling results in temporary incapacity to foam.
- (2) Chilling effect is eliminated by long standing or by heating above 50° C.
- (3) Precipitation of crystalline or waxy material is observed.
- (4) Chilling effect is less pronounced when the precipitate is removed.
- (5) Addition of mechanically separated precipitate to normal oil causes no change in its foaming tendency.

D. Solvent Extraction.— Four samples of lubricating oil in various states of the refining process were obtained from the Union Oil Co. These were labeled:

- (1) Before propane extraction
- (2) Before solvent extraction
- (3) Before clay treatment
- (4) After clay treatment, but without any additive

These oils were subjected to room temperature foaming tests. Samples (1) and (2) had a high foaming capacity, whereas the foams produced with samples (3) and (4) were both small in volume and unstable, indicating that most of the foaming constituent (or constituents) have been removed during the

process of solvent extraction. The clay treatment resulted in some improvement, though the bulk of the effect occurs in the extraction by solvent (phenol).

A number of samples illustrating the propane solvent process were obtained from the Union Oil Company. Among them was a sample of solvent extract, which when added to a completely refined oil (Union) caused a marked increase in the foam stability both at room temperature (23° to 25° C) and at 100° C. When cooled to about 15° C, the oil foamed the same as originally (as noted in the section on Chilling).

Samples of propane precipitated waxes and of propane precipitated resins were also tested in a similar manner, but were found to have only a very slight effect in comparison with the solvent extract.

The samples tested; namely, the waxes, resins, and the solvent extract, represent the type of impurities generally removed in refining lubricating oils. It has been shown that the waxes and resins do not affect the foamability of a refined oil to any marked extent.

The phenol extract supplied by the Union Oil Company contains some constituent that favors foaming: as shown above, the extract greatly increases the foaming tendency of a refined lubricating oil. The completely refined product of this company foams considerably less than before refining, and slightly less than Aeroshell 120, Gulf Air-line 120, and NACA reference oil 120. The differences may partly be due to different solvents used in refining.

Laboratory extraction of refined oils with phenol has only begun. In a single experiment with NACA reference oil, 30 grams of phenol were added to 100 grams of oil at room temperature. The mixture was heated to melt the phenol and then shaken vigorously for several minutes. The resulting emulsion was centrifuged in a small angle centrifuge in an oven at 60° to 70° C, so as to maintain the phenol in a liquid state. Even after 1 hour, only a small amount of the phenol separated. The remainder was allowed to crystallize, after which it was filtered from the oil. Of course, crystallization of the phenol might well release to the oil anything dissolved in the liquid phenol.

The phenol extracted oil was then tested for foaming by the aeration-evacuation method. In this first test there was no distinct difference between the reference oil and the

treated sample. However, the technique of phenol extraction is being improved and further work along this line is planned.

E. Segregation in the Interface with Water.— This experiment involved the extraction of some constituent by slowly dropping water through a long column of oil. An ordinary 50-millimeter burette was filled with Aero-shell 120. The flow of water from a reservoir at the top of the burette was regulated so that the droplets remained completely independent of one another. In this way a maximum surface exposure was obtained. This process was allowed to continue for several days, the water being drained off intermittently at the burette tip.

Evidence of successful extraction by this method is that the treated oil foamed considerably less than a corresponding control sample. Furthermore, the fact that bulk extraction with water fails to change the foaming tendency of this oil indicates that the constituent removed does not dissolve in the water, but rather is concentrated at the water-oil interface and is so removed from the oil.

Summary

Five methods have been used in the attempt to remove foaming constituents from lubricating oils. These include:

1. Segregation of the constituent in the foam.
2. Adsorption on an active surface.
3. Chilling and filtration.
4. Solvent extraction.
5. Segregation at the water-oil interface.

In the foam segregation experiments, two positive results are reported. Oil which had been treated with activated charcoal had a lower refractive index than the corresponding untreated oil. Chilling of various oils, both new and used, resulted in a temporary loss of foaming ability, which is restored on long standing or on heating. A commercial solvent extraction process using phenol leads to a distinct improvement in foaming characteristics: furthermore, the addition of the solvent extract to the refined

product markedly increases the foaminess. Slowly dropping water through oil in a long column also resulted in a decreased foam stability.

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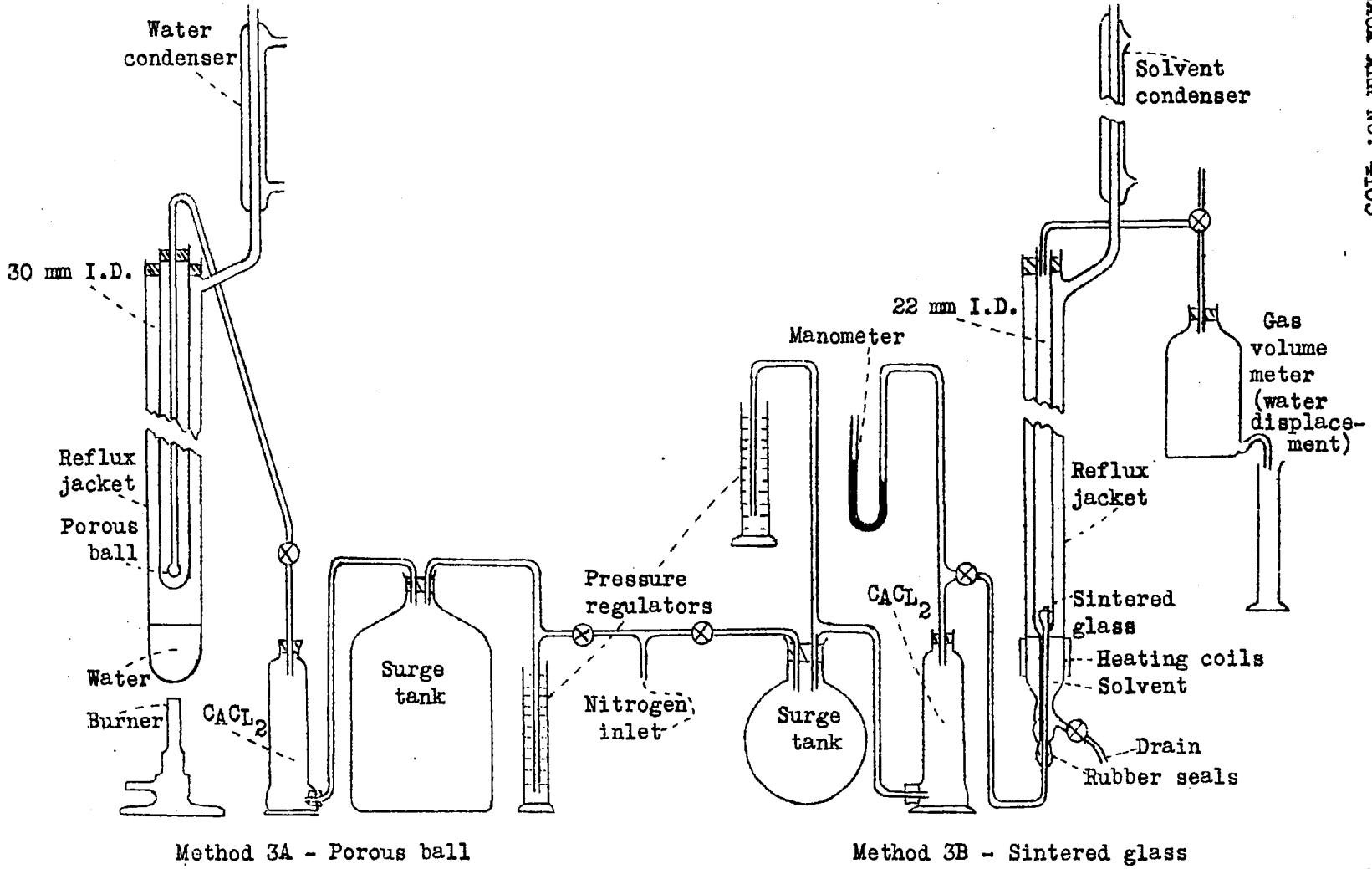


Figure 1.- Bubbling foam meters for various temperatures.

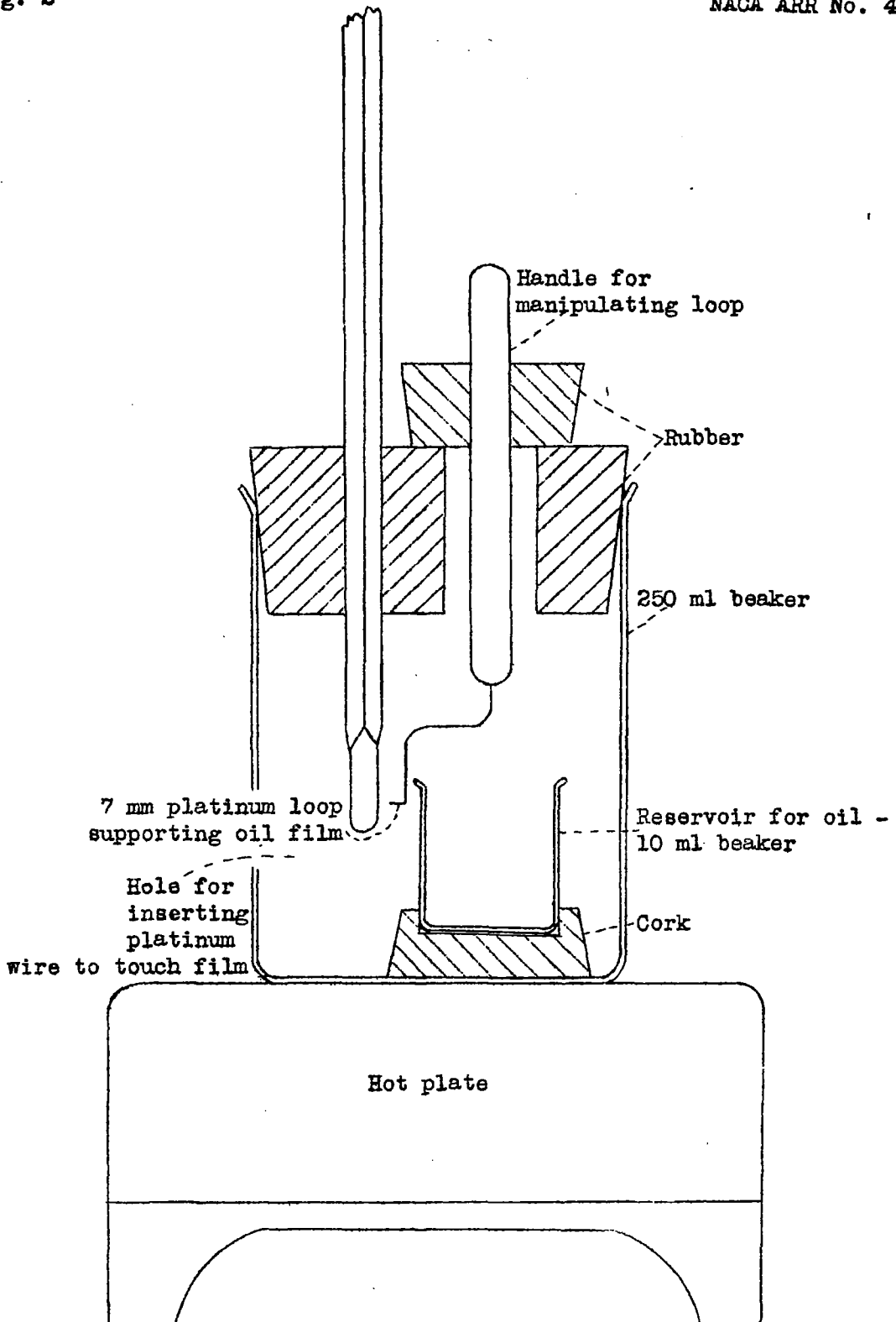


Figure 2.- Film break or "Pop test" apparatus.

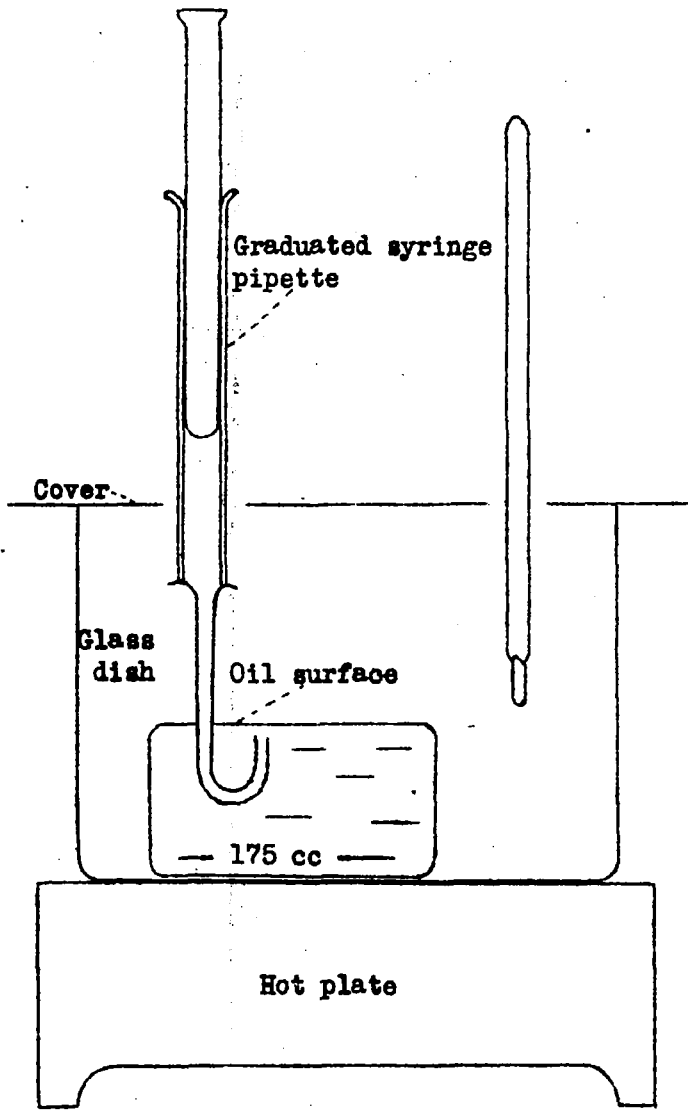


Figure 3.- Single bubble apparatus.

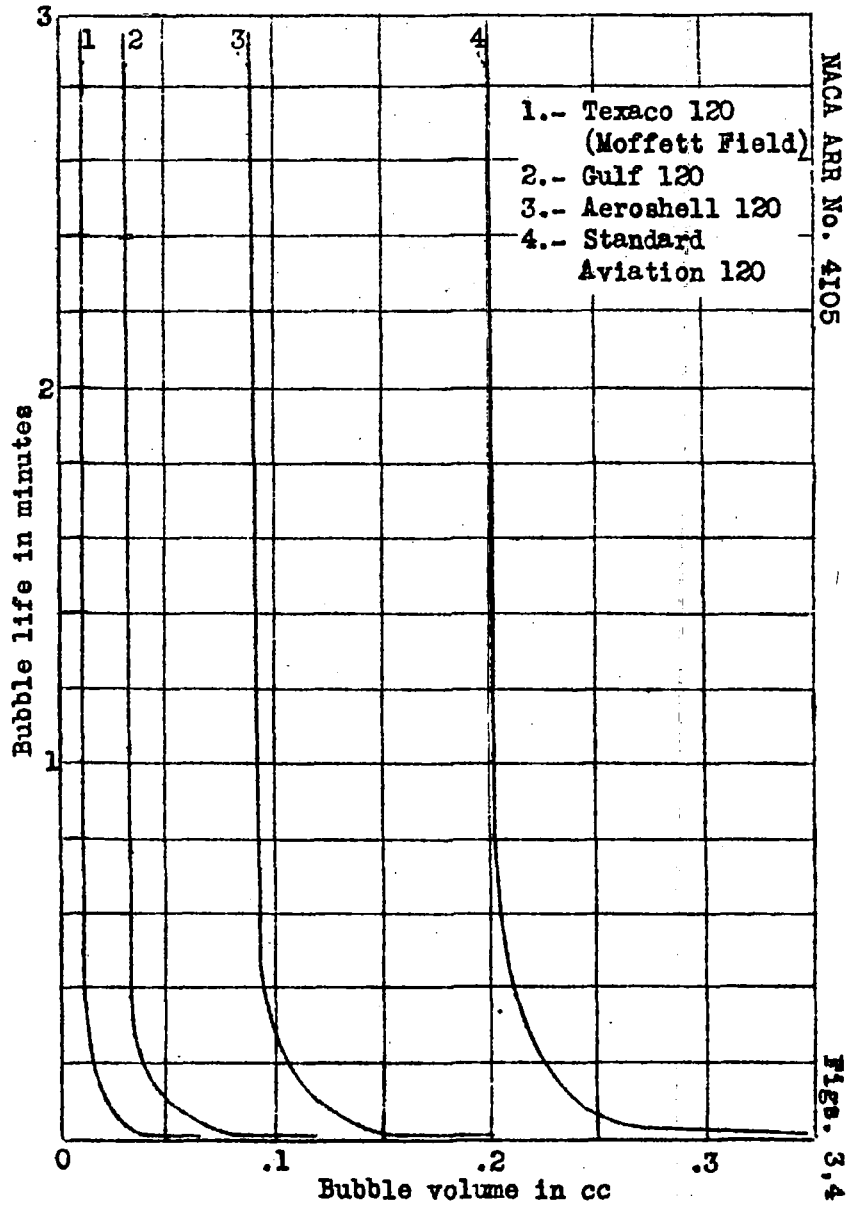


Figure 4.- Single bubble stability.

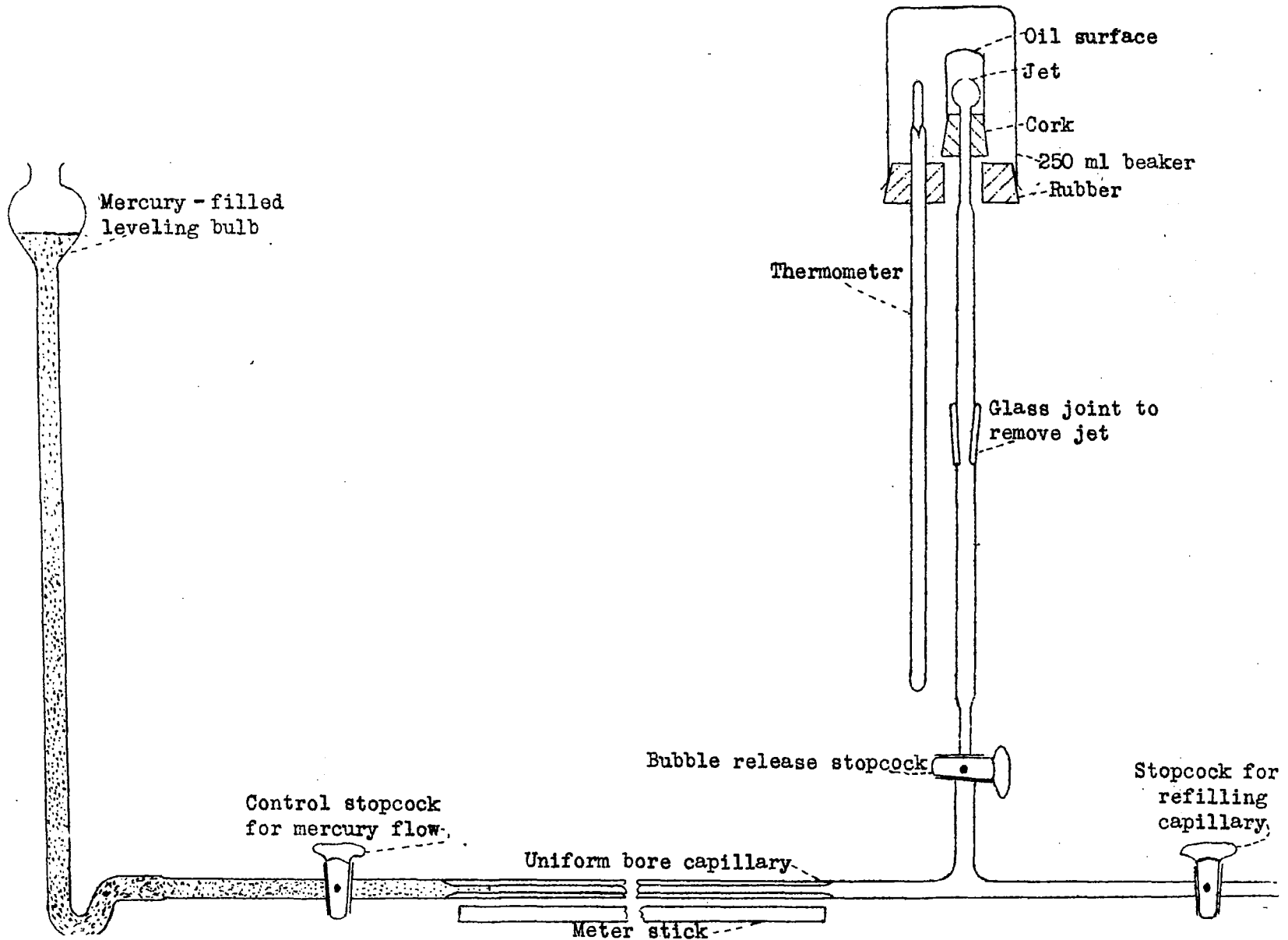


Fig. 5

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Figure 5.- Modified single bubble apparatus.

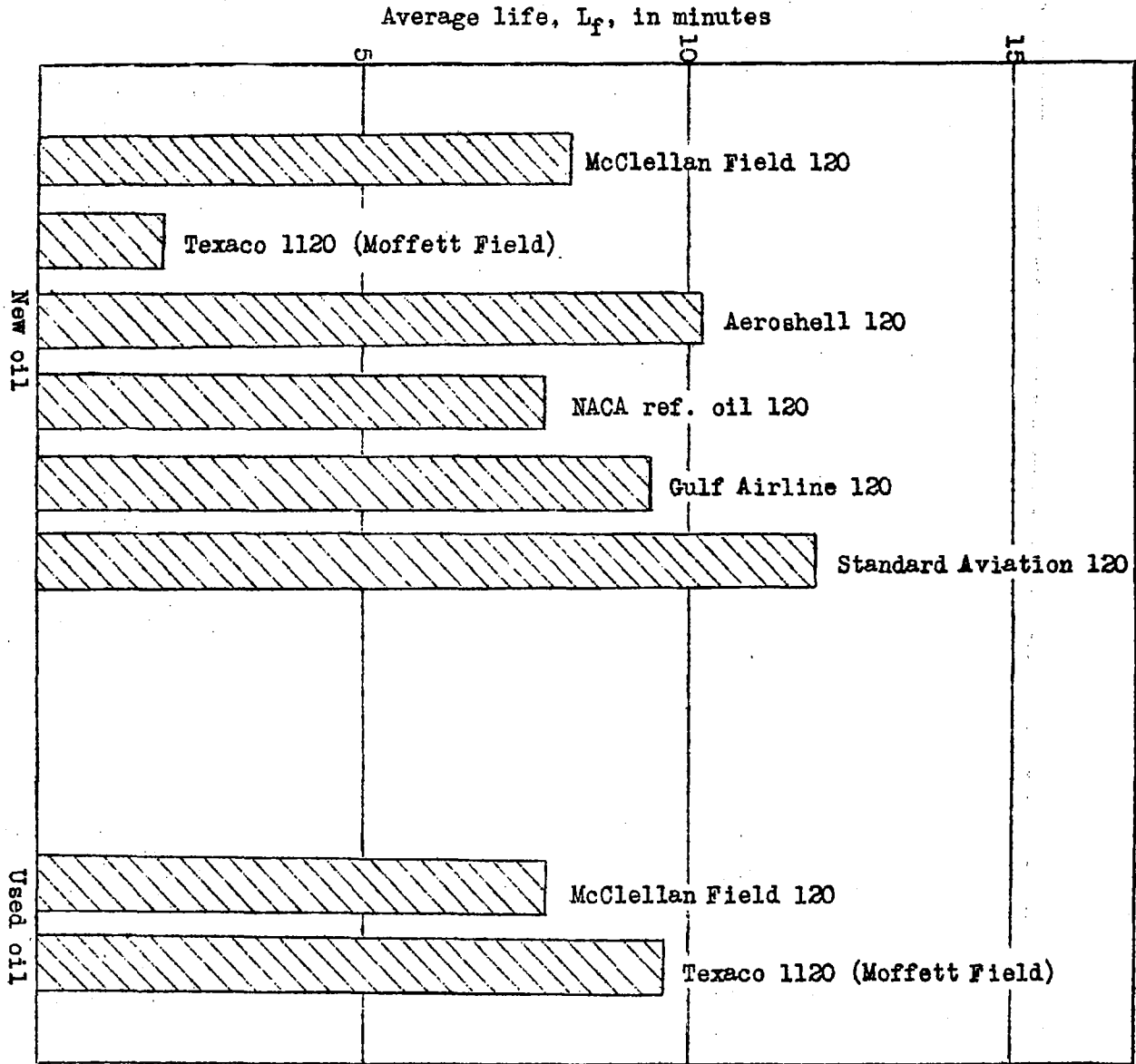


Figure 6a.-- Average life of oil foam at room temperature (aeration and evacuation).

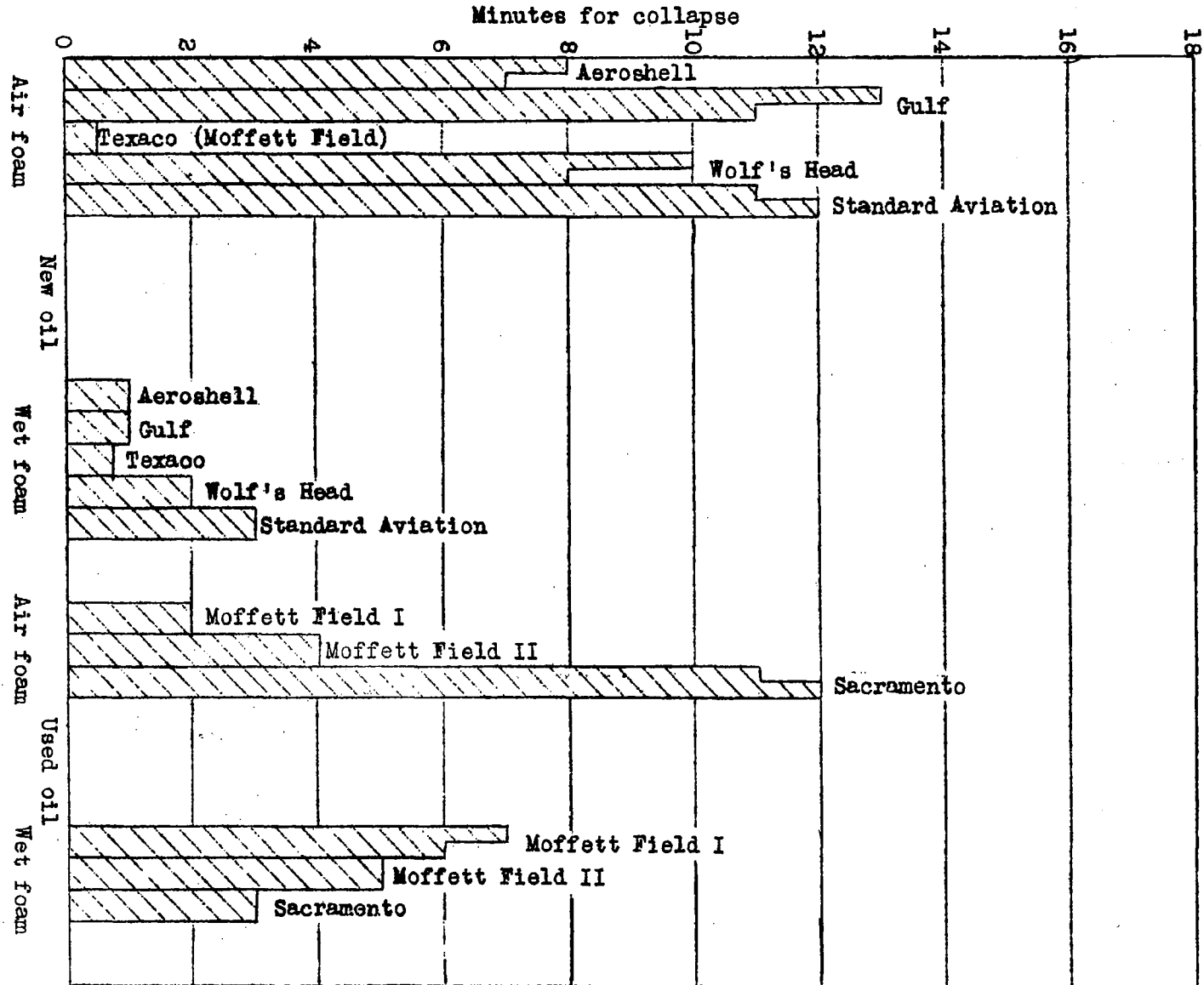


Figure 6b.-- Time taken for 200 cc of froth to collapse at room temperature.

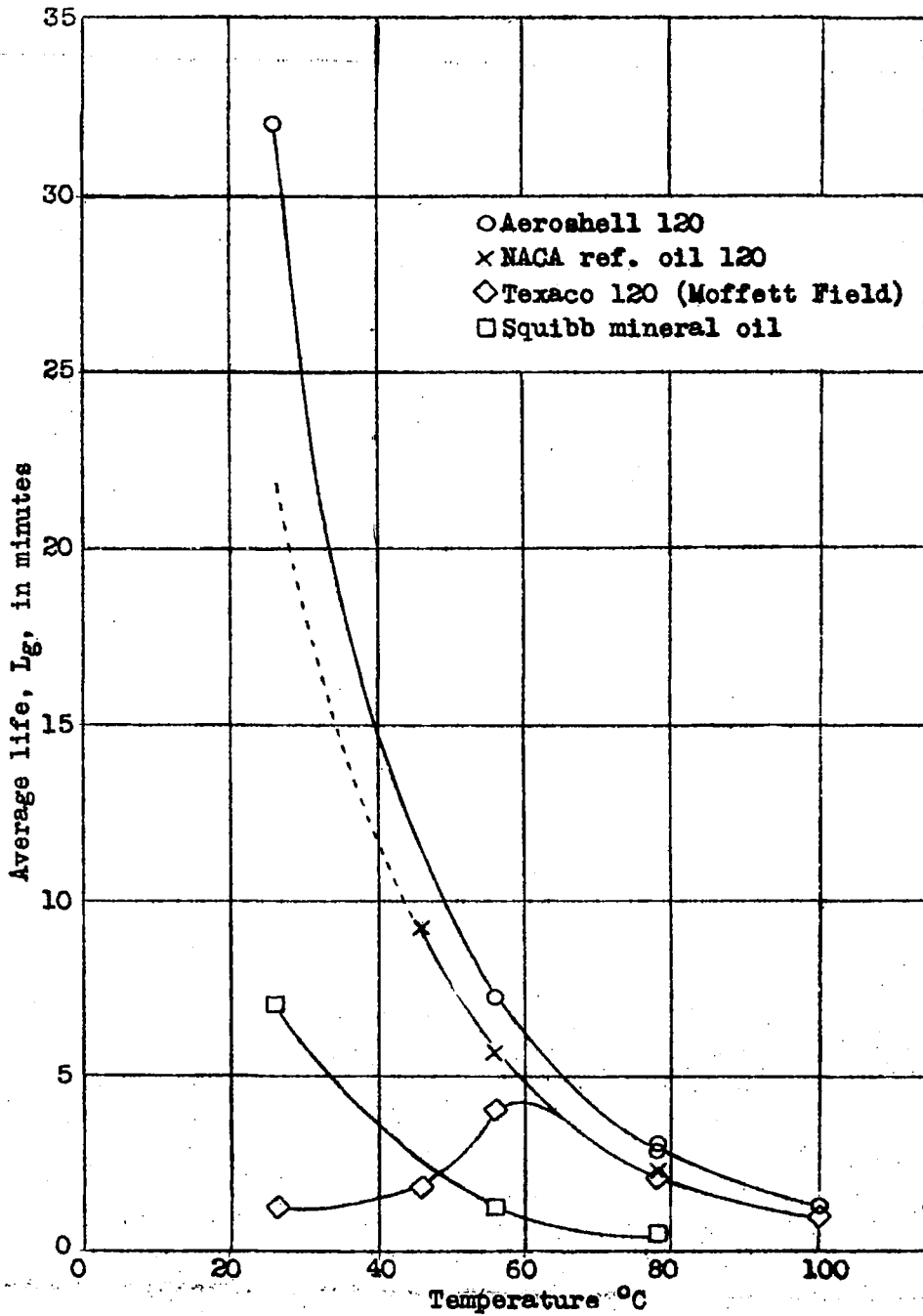


Figure 7a.- Average life of gas in foam against temperature in $^{\circ}\text{C}$.

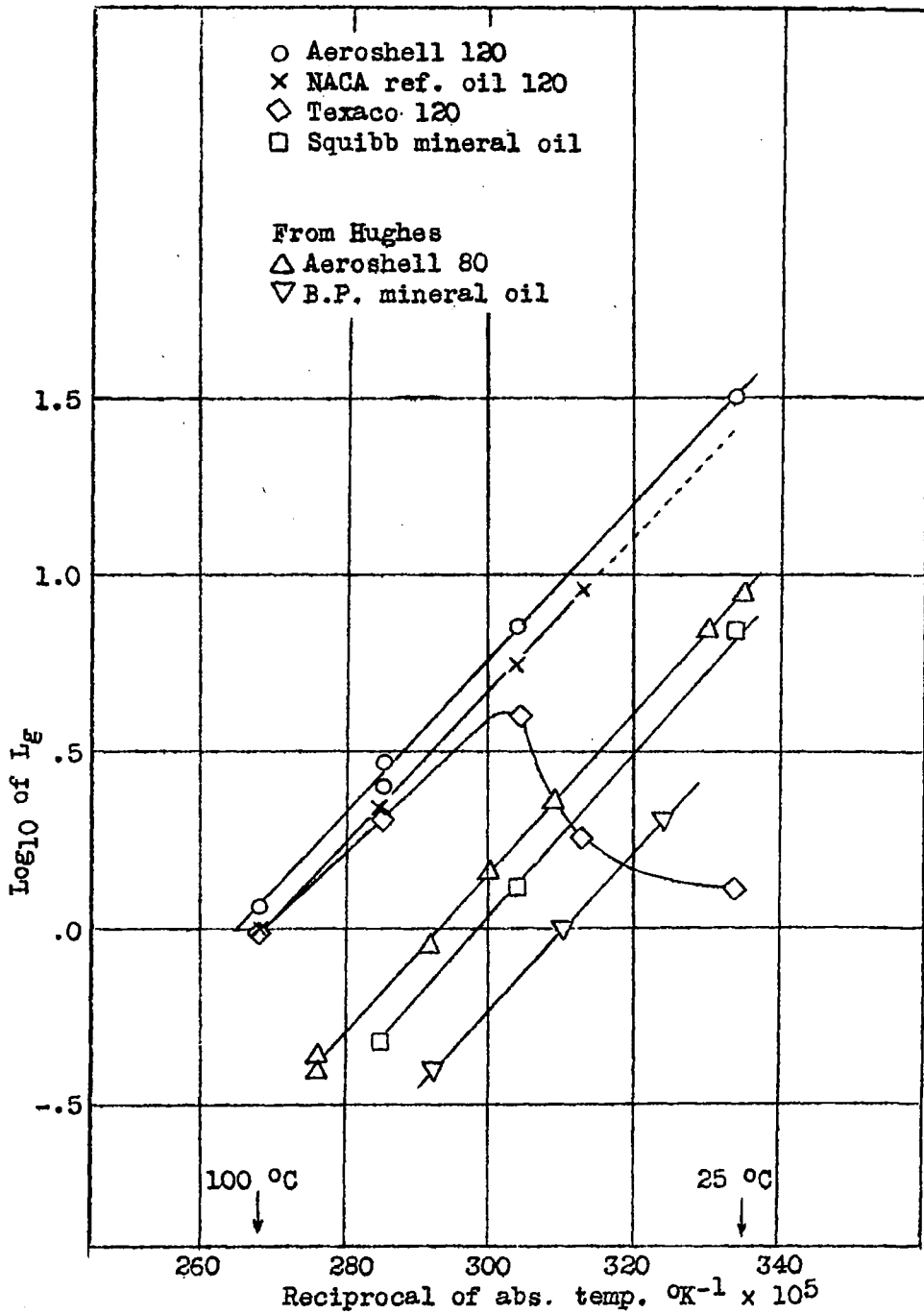


Figure 7b.- Log of average life of gas in foam against reciprocal of abs. temp. in $^{\circ}\text{K}^{-1}$.

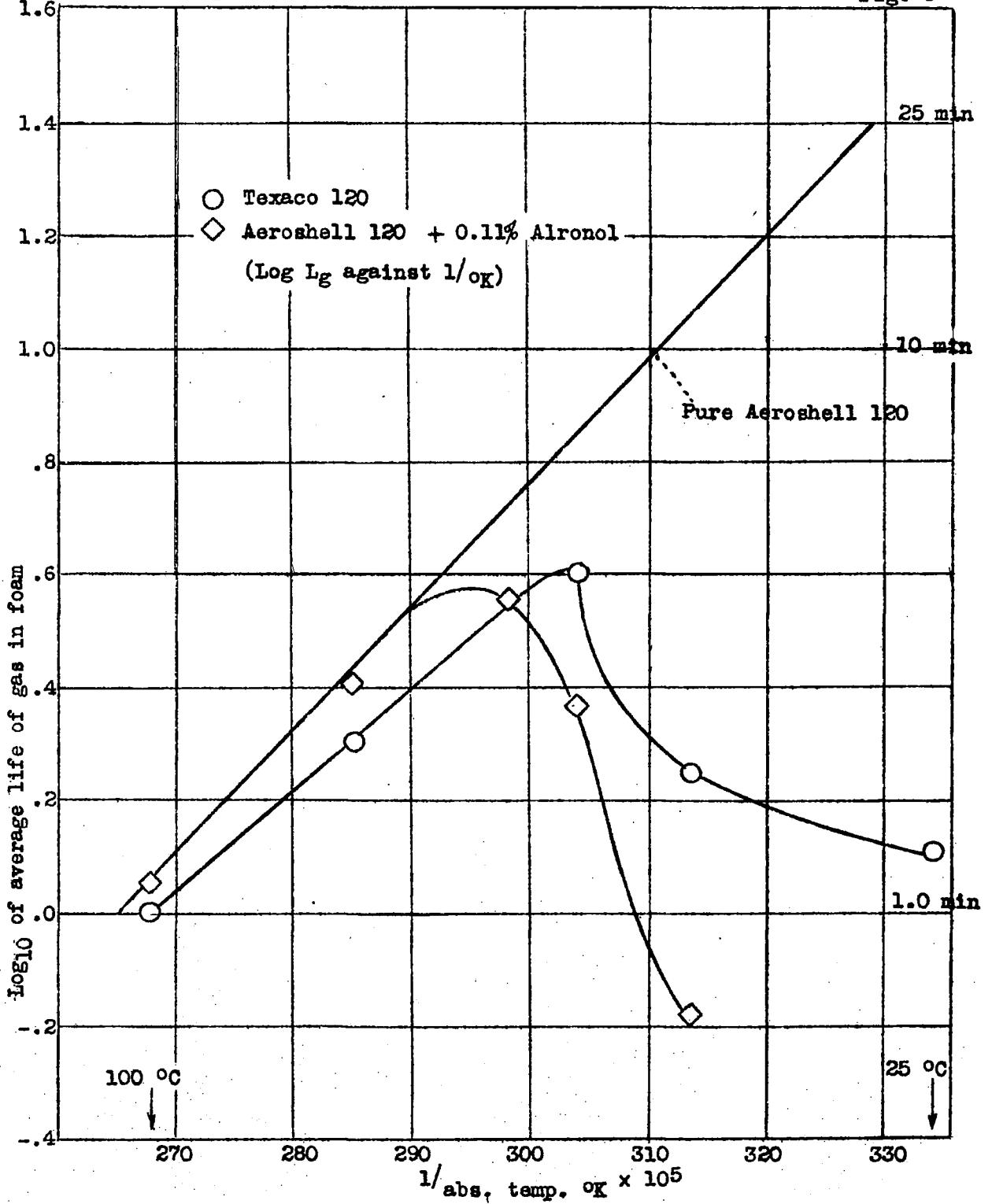


Figure 8.- Comparison between Texaco 120 from Moffett Field and Aeroshell 120 + 0.11% Alronol.

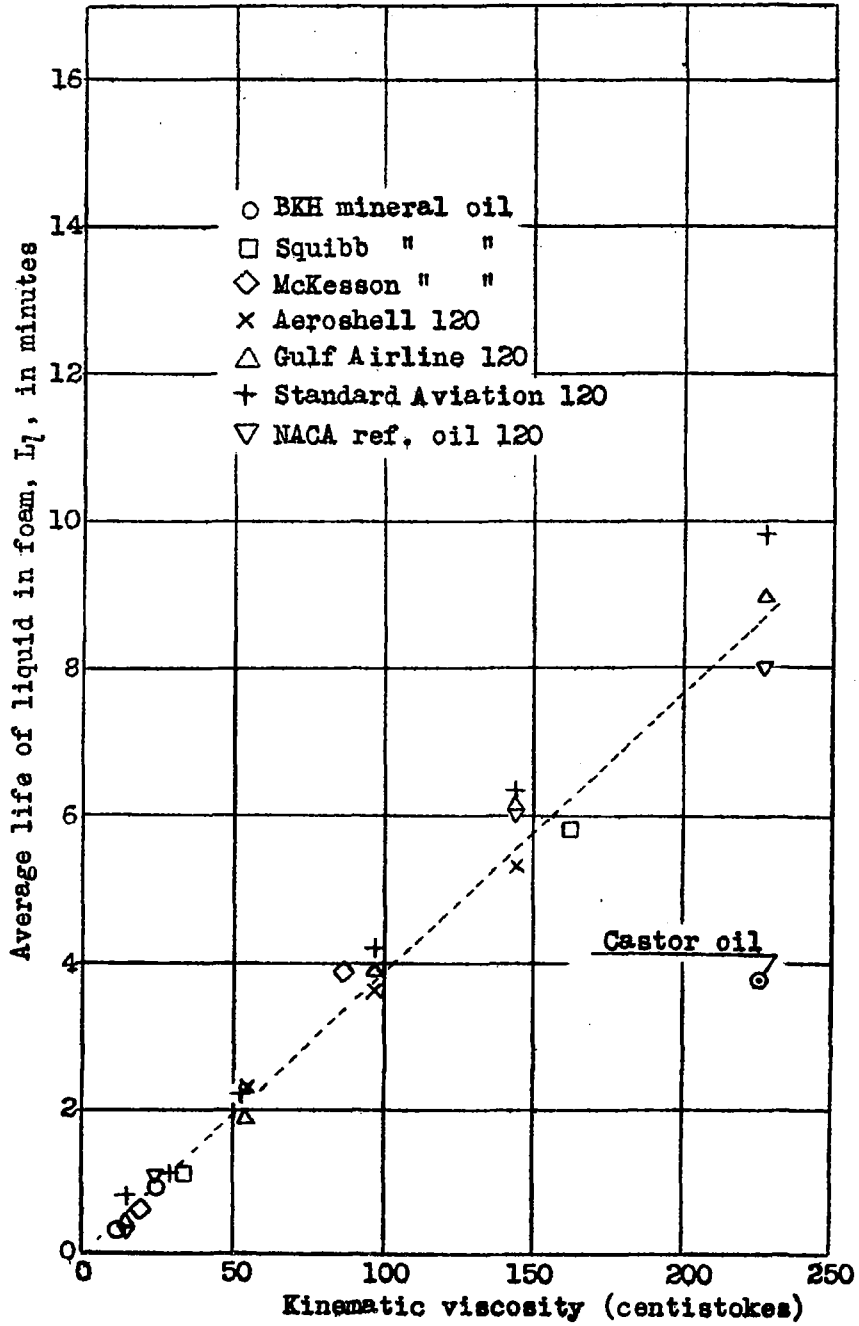


Figure 9a.- Average life of liquid in foam against kinematic viscosity.

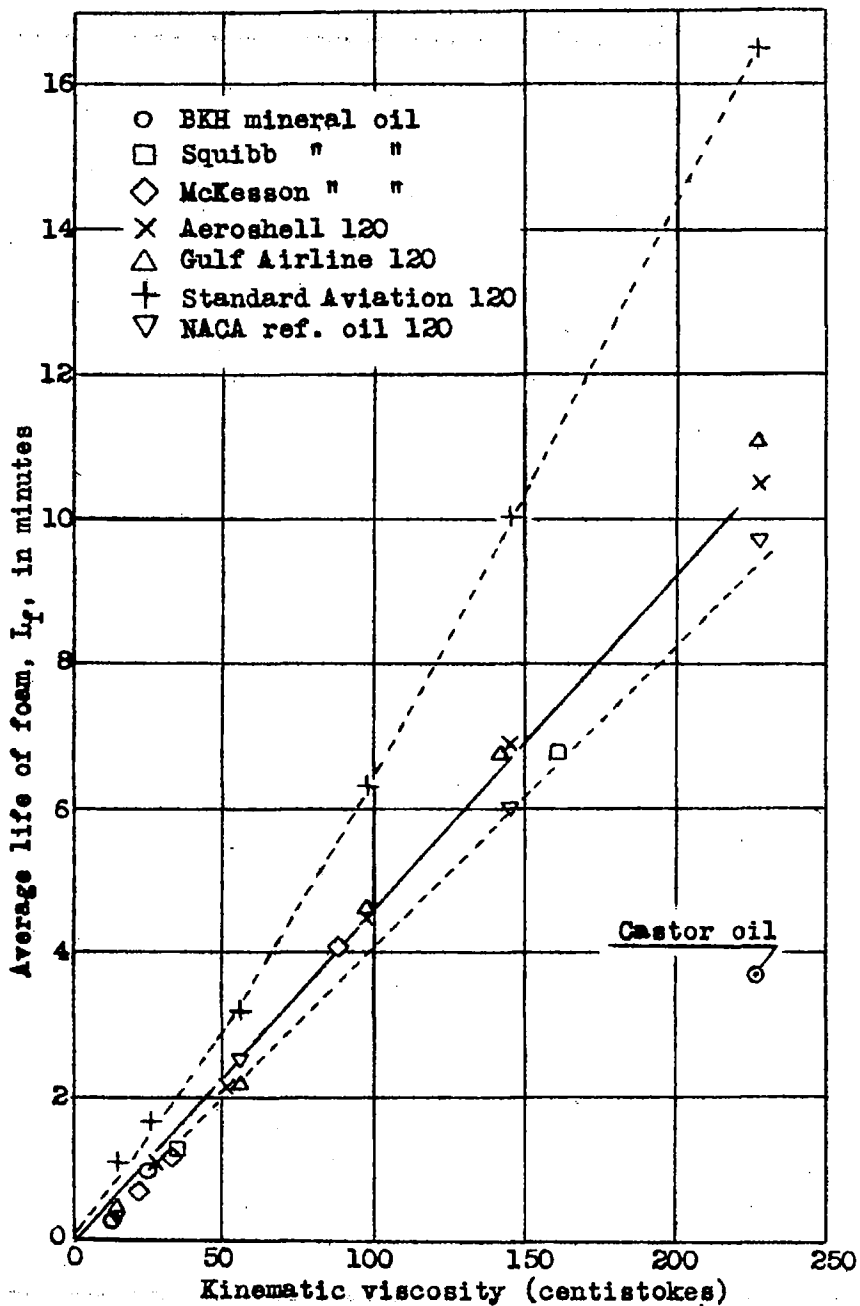


Figure 9b.- Average life of foam against kinematic viscosity.

Fig. 10

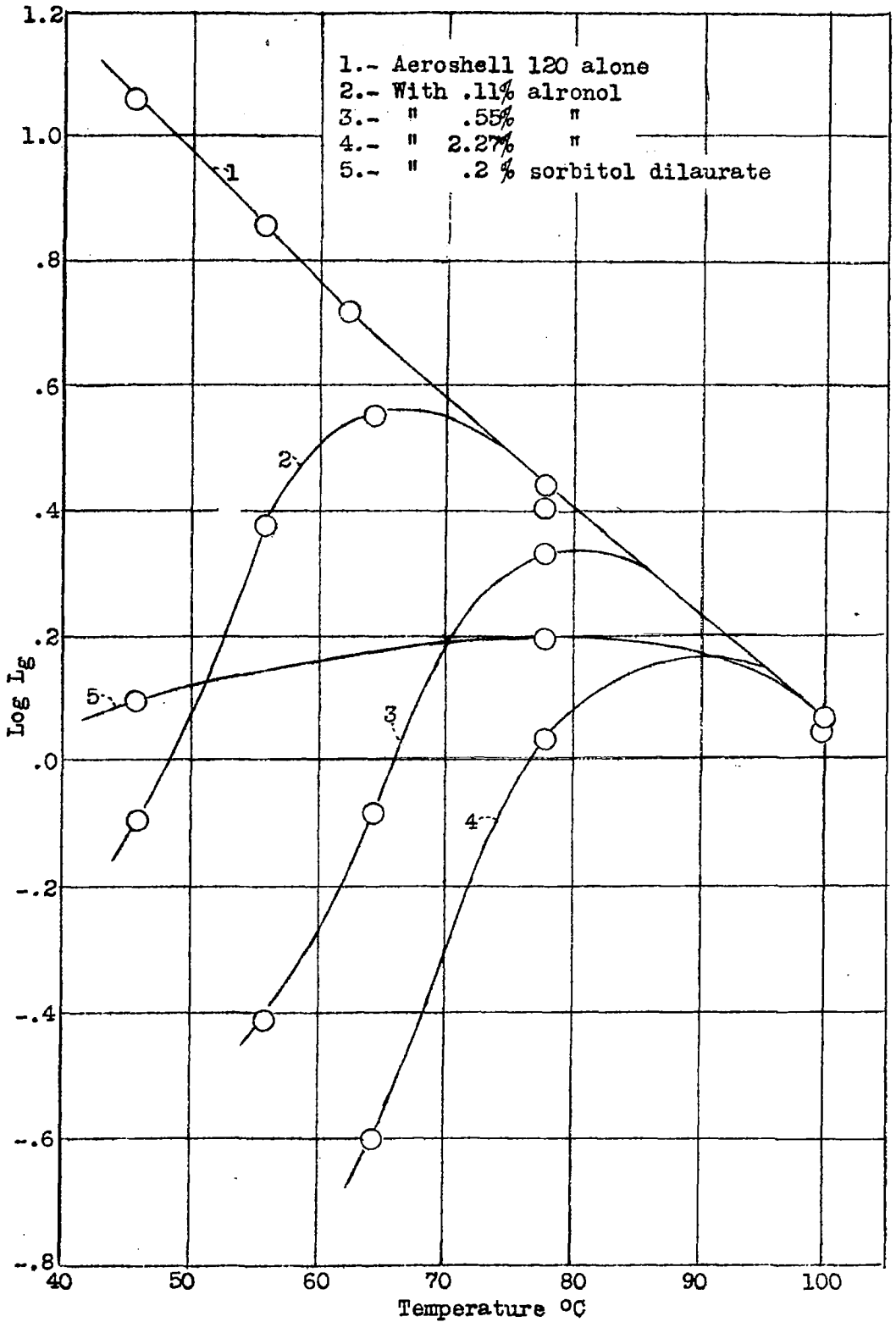


Figure 10.- Effect of temperature on antifoamers.

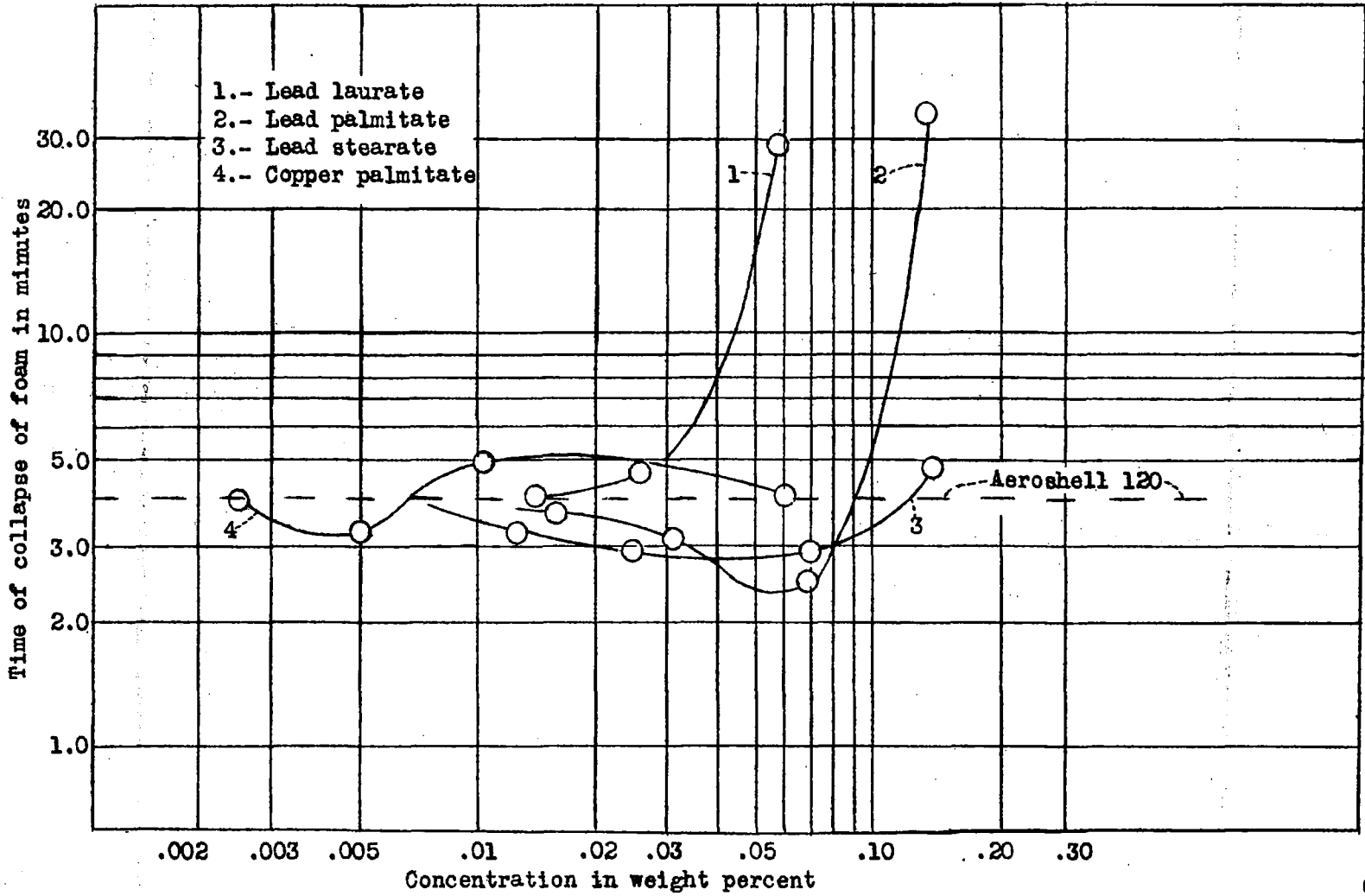


Figure 11.- Effect of concentration of antifoamers at 100 °C.

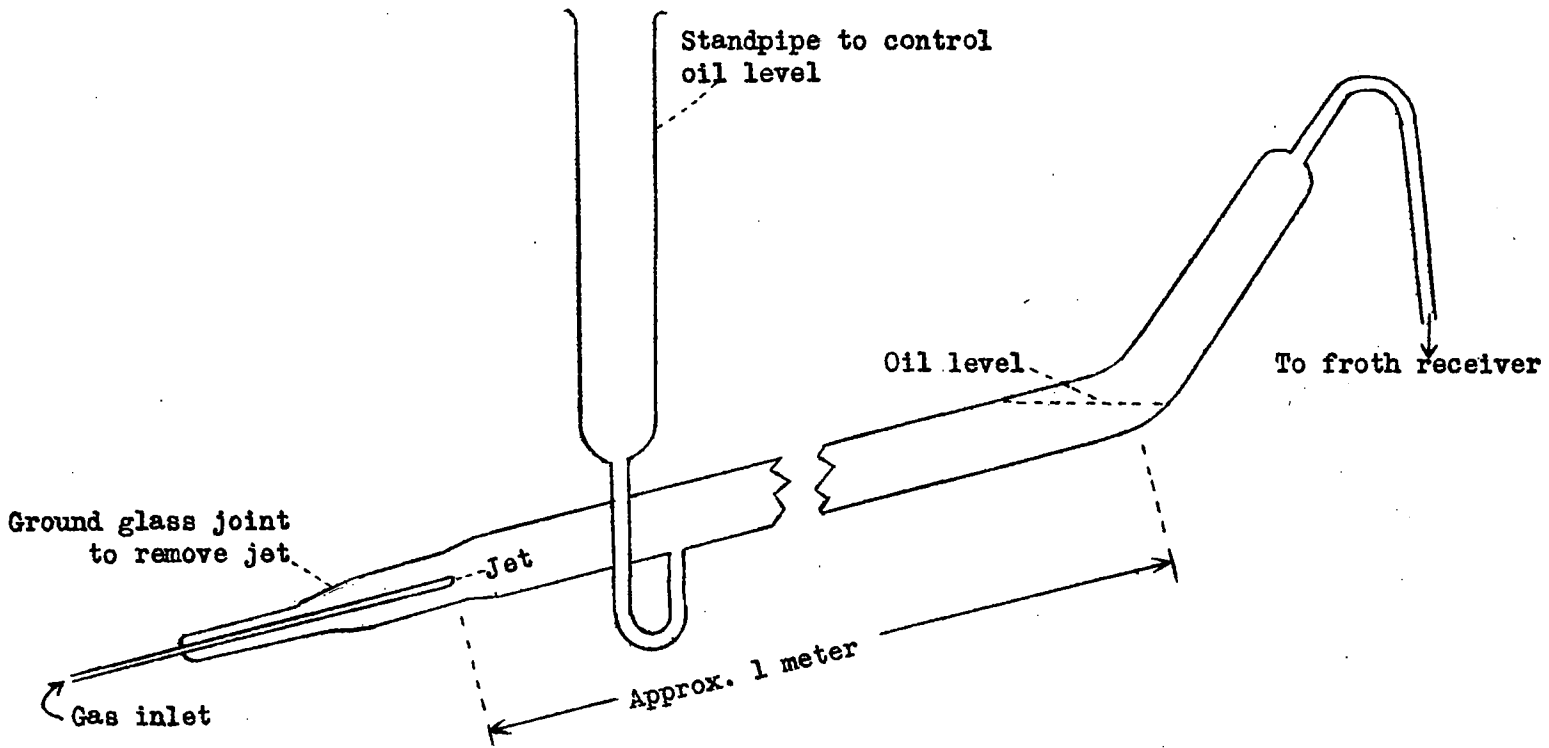


Figure 12.- Froth segregation apparatus.

FORM 10 (13 FEB 47)

McBain, J. W.
Ross, S.

DIVISION: Power Plants, Reciprocating (6)
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ABSTRACT

Efforts to produce an adequate theory of foaming of engine lubricants were unsuccessful. Impurities of unknown character may be the cause. A number of substances are listed capable of preventing or minimizing foaming of oils. Tests point to a nonexistence of either a universal foaming, or a universal antifoaming agent. Manner of producing foam and environment affect stability of foam. Lifetime of air supported film in normal engine oil varies between 3 sec and 1 hr.

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