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TECHNICAL NOTE

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QUANTITATIVE STUDY OF VARIATIONS IN CONCENTRATION OF
GLYCEROL AND AEROSOL OIL ON FOAMING VOLUME OF

OIL AT ROOM TEMPERATURE

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Stanford University

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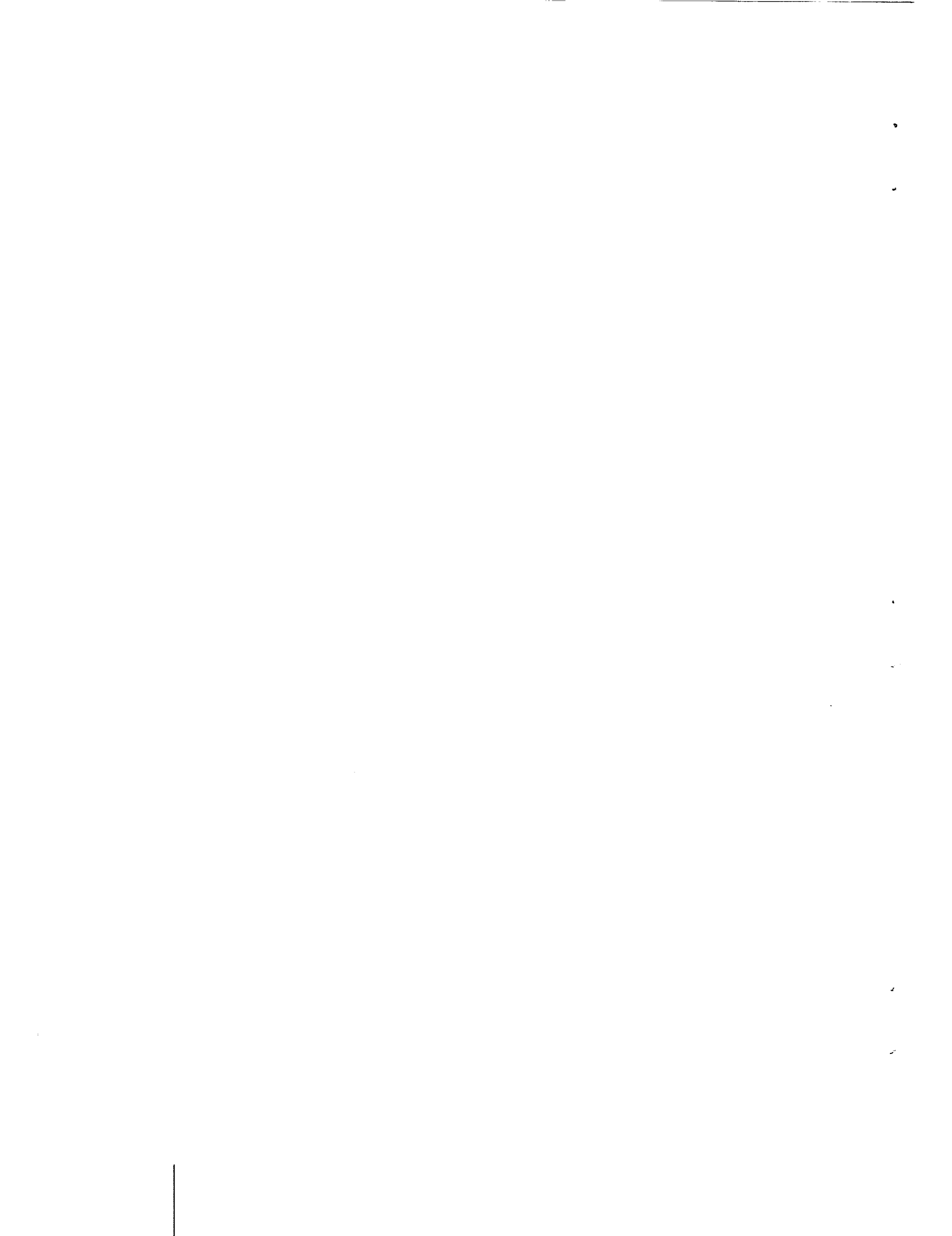
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QUANTITATIVE STUDY OF VARIATIONS IN CONCENTRATION OF
GLYCEROL AND AEROSOL OT ON FOAMING VOLUME OF
OIL AT ROOM TEMPERATURE

By J. W. McBain and Sydney Ross

SUMMARY

The amount of foam that can be formed in the presence of certain pure chemical agents was investigated by a new method. The effect of variations in concentration and proportion of Aerosol OT and glycerol was studied and the effects of various other mixtures have been given for comparison.

Both Gulf Agent and Aerosol-OT - glycerol mixtures, when present in comparable amounts, prohibited the formation of the normal volumes of foam to the same extent and in the optimum cases reduced it to only one-tenth of its normal value.

INTRODUCTION

The effects of known mixtures of chemicals on the foaming of oils have been previously reported (see reference 1). The test most extensively used consisted of bubbling gas through a porous clay ball into the oil at elevated temperatures and noting whether foam could be formed under those conditions in the presence of known amounts of pure added chemical. Tests of other types have since been conducted, including the method of beating and evacuation at room temperature (qualitative), the method of beating the oil at room temperature (quantitative), and the bubbling method at 100° C (quantitative).

This program of research was conducted at Stanford University under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

METHOD OF TEST

The determination of foam-inhibiting capacity cannot be readily carried out by many of the methods previously reported because the production of a suitably large amount of foam is not generally possible

when antifoaming agents have been added. Consequently, a new method was devised. The following specifications have been found in practice to give satisfactory results.

Two hundred and fifty cubic centimeters of the oil is circulated in a colloid mill until the temperature rises through friction to 110° C. The mixture to be tested is then added from a volumetric pipette and the mixing in the colloid mill continued for 20 minutes. The sample is then bottled and allowed to cool to room temperature. The behavior of the oil in the colloid mill after the addition of the mixture gives valuable information concerning the effect of the mixture on oil at higher temperatures. A room-temperature test is next conducted. Ninety grams of the sample is weighed and stirred for 3 minutes by an electric kitchen mixer at full speed. The blades are allowed to drain for 15 seconds and the foam is then rapidly passed into a previously weighed graduated cylinder. Exactly 100 cubic centimeters of the foam is transferred and weighed. In the case of excellent defoaming agents, it is not always possible to obtain as much as 100 cubic centimeters of foam, and in those cases exactly 90 cubic centimeters of the foam is taken and its weight calculated as for 100 cubic centimeters. Since the oil used throughout the experiments is Aeroshell 120, which has a density of 0.88 gram per cubic centimeter at 30° C, if no air were present in the oil the 100-cubic-centimeter sample would weigh 88 grams. Actually, because of the presence of air, the weight of 100 cubic centimeters of foam is less than 88 grams. The difference between 88 grams and the actual weight of the foam is the weight of oil supplanted by air in 100 cubic centimeters of foam. Dividing by 0.88 gives the percentage volume of air in the foam and hence is a measure of the amount of foam that can be formed under the conditions of the test. It is the percentage of air enclosed in the oil, the frothing value as defined in reference 2 under Total Foam Volume and Its Practical Significance.

Many other numerical forms of expression are possible. The weight of oil supplanted by gas in the foam can be converted into the corresponding volume, which is also the volume of gas in the foam. In turn, this value can be converted into foam density, volume increase, percentage volume due to entrained air, or total amount of foam.

INVESTIGATION OF METHOD OF BEATING TO OBSERVE

PERCENTAGE OF ENTRAINED AIR IN OIL

When the directions previously specified are followed at a temperature of $25^{\circ} \pm 1^{\circ}$ C, values for Aeroshell 120 range from 51.1 to 51.7 cubic centimeters of air per 100 cubic centimeters of total oil and foam. The variations in the specifications of the method investigated were as follows:

- (a) Variation of length of time of beating
- (b) Variation of interval elapsed after beating before pouring
- (c) Variation in depth of immersion of blades (i.e, initial volume of sample)
- (d) Variation in speed of beating
- (e) Variation in degree of previous aeration of oil sample

All these tests were performed on Aeroshell 120 at temperatures of $25^{\circ} \pm 1^{\circ} \text{C}$ and the results are given in table I. This table reveals the factors significant for reproduction of results by this test. With aviation-lubricating-oil samples of ordinary viscosity (SAE 60) the froth remains homogeneous after beating at room temperature for more than 60 seconds; hence slight variations in the time elapsed before pouring the froth into the measuring cylinder will have no effect on the result.

Variations in the time of beating at full speed do not affect the final amount of air entrained in the oil; hence an equilibrium can be presumed to be established in the beating process. At low speeds this equilibrium value or steady state shifts in the direction of the entrainment of more air than was entrained at the highest speed. The difference in entrainment at different speeds is not great but nevertheless shows that the more rapidly moving parts actually break up the foam to some extent. The direct test, in which a more voluminous foam formed by bubbling was beaten, showed that the volume was reduced to the same equilibrium value or steady state.

The degree of immersion of the blades in the sample is a critical factor; the greater the immersion, the more air can be entrained in the final foam. For this reason the part of the specifications that requires the greatest attention is the weighing of the amount of sample taken. Identical vessels should also be used for all the beating tests to ensure the same degree of immersion of the blades throughout.

This test has been used not only to investigate the effect of anti-foaming agents but also to characterize various oils (reference 2, table I).

RESULTS

The first part of this section presents information on the relative effectiveness of different concentrations and amounts of a mixture of Aerosol OT (dioctyl sodium sulfosuccinate) and glycerol. The oil used

throughout the tests is Aeroshell 120, an aviation lubricating oil without any additives or pour-point depressant. For comparison, Aeroshell 120 alone gives a value of percentage air entrained or frothing volume equal to 51.4 percent. (See table II.)

The presence of triethanolamine oleate in addition to the other two chemical agents enhances the antifoaming effect to a slight degree, as shown in table III.

For comparison, the effect of different concentrations of the Gulf Oil Corporation's defoaming concentrate is given in table IV. The greatest effect occurs at a concentration comparable with those at which effects of the same order of magnitude can also be achieved with the antifoaming mixture already described (Aerosol-OT - glycerol mixture) and other mixtures still to be mentioned.

Some experiments were also undertaken to determine whether the efficiency of the Gulf Oil Company's agent could be improved by additions of other known chemical agents. A comparison of the results obtained is provided in table V.

QUANTITATIVE RESULTS AT 100° C WITH SODIUM AEROSOL OT PLUS GLYCEROL

An extensive survey of the influence of the concentrations of these constituents on foam inhibition in Aeroshell 120 has been made at room temperature (reference 2). During this investigation the effect of temperatures of approximately 100° C was estimated from the behavior in the colloid mill during the mixing process. As a check, a few samples were tested directly at 100° C in the porous bubbler foam meter. From table VI, it can be seen that the quantitative experiments by the bubbling method completely corroborate the qualitative observations in the colloid mill.

ANALYSIS AND DISCUSSION

The determination of the frothing volume has already been discussed in reference 2. A method is described herein and used for the determination of the percentage air entrained, frothing volume. The method is herein chiefly used for the investigation of the effect of known mixtures of pure chemicals, and the numerical results reported are an indication of the action of the additive on the amount of foam formed with no information about its stability. It seems certain that, if the amount of foam that is capable of forming is reduced to a very low value, the intrinsic stability of the small volume of foam will be of little concern.

In the Aerosol-OT - glycerol mixtures, variation of the proportions and concentrations within wide limits apparently does not have any critical effect on the amount of foam. The smallest amount of air that is entrained (3.2 percent) is obtained with 200 parts per million of glycerol plus 200 parts per million of Aerosol OT. For comparison, 500 parts per million of the Gulf Agent entrains 3.6 percent of air, and 50 parts per million of the Gulf Agent entrains 6.5 percent of air. The addition of a small quantity of triethanolamine oleate can enhance the effect of the Aerosol-OT - glycerol mixture to a value as low as 2.8 percent of air entrained, although the sum of the concentrations of the three agents is 1200 parts per million; the small gain in effect probably is hardly worth the large increase of concentration necessary to produce it.

An attempt to improve the effect of the Gulf Agent by addition of either glycerol or Aerosol OT, or both, was unsuccessful. Unless the Gulf Agent is present in a concentration of approximately 500 parts per million, even small amounts of Aerosol OT and/or glycerol are deleterious to its normal action. Although effective separately as antifoaming agents, the presence of one lowers the action of the other.

Although the effect of one mixture in particular (Aerosol OT and glycerol) has been extensively investigated, there are other similar mixtures that have already provided strong indications of equal effectiveness. These mixtures have been studied by the quantitative method for amount of foam to only a limited extent thus far, although that method has already shown itself to be of great value for a final judgment of any mixture. The method may also be of value in obtaining some generalizations concerning structure and foam-inhibiting action, as, for example, the interesting result (reference 3) of the greater effectiveness of the long-chain alcohol C_{17} over that of the shorter chain C_8 when sodium salts of sulfated alcohols are used.

SUMMARY OF RESULTS

A quantitative method for measuring the frothing volume on beating oil, the percentage of air entrained, or the amount of foam has been described, investigated, and used.

Aerosol-OT - glycerol mixtures were shown to be effective in reducing the percentage of air entrained to less than one-tenth of its normal volume when present in total amounts of 400 parts per million. The same effect is obtained with Gulf's Agent in concentrations of 500 parts per million. Concentrations of Gulf Agent much lower than 500 parts per million caused a reduction in the desired effect.

Stanford University

Stanford University, Calif., January 8, 1945

REFERENCES

1. McBain, J. W., Ross, S., Brady, A. P., Robinson, J. V., Abrams, I. M., Thorburn, R. C., and Lindquist, C. G.: Foaming of Aircraft-Engine Oils as a Problem in Colloid Chemistry - I. NACA ARR No. 4105, 1944.
2. McBain, J. W., Ross, Sydney, and Brady, A. P.: Analysis of Properties of Foam. NACA TN No. 1840, 1949.
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TABLE I. - VARIATIONS IN SPECIFICATIONS OF METHOD

Treatment	Frothing volume (percent air in foam)	Comment
Specified in test	51.5	Control
Beaten at full speed for 30 minutes instead of 3 minutes	51.3	No difference
Foam measured immediately after beating instead of 15 seconds after	51.1	No difference
Foam measured 60 seconds after beating instead of 15 seconds after	51.4	No difference
Oil turned to froth by bubbling for 24 hours before testing	51.7	No difference
Initial volume of sample taken as 76 grams of oil instead of 88 grams	47.9	Lower value
Initial volume of sample taken as 144 grams of oil instead of 88 grams	54.7	Higher value
Beaten at one-half speed for 3 minutes instead of at full speed	55.2	Higher value
Beaten at low speed for 15 minutes instead of at full speed for 3 minutes	54.6	Higher value

TABLE II.- VARIATION IN CONCENTRATIONS OF AEROSOL OT
AND GLYCEROL IN AEROSHELL 120

In proportion of 1:3			
Total added (percent)	Glycerol (ppm)	Aerosol OT (ppm)	Air entrained (percent)
0	0	0	51.4
.04	300	100	4.3
.06	450	150	3.5
.08	600	200	3.5
.10	750	250	3.4
.12	900	300	4.7
.16	1200	400	4.3
In proportion of 1:2			
0.02	133	67	6.6
.04	267	133	4.6
.06	400	200	4.5
.08	533	267	4.6
.10	667	333	7.4
.12	800	400	4.5
In proportion of 1:1			
0.02	100	100	5.1
.04	200	200	3.2
.06	300	300	12.2
.10	500	500	18.9
.14	700	700	20.9
.20	1000	1000	20.7
.40	2000	2000	22.7

TABLE III.- INCREASED ANTIFOAMING ACTION DUE TO PRESENCE OF
TRIETHANOLAMINE OLEATE ON AEROSOL-OT - GLYCEROL MIXTURE

Total added (percent)	Glycerol (ppm)	Aerosol OT (ppm)	Triethanolamine oleate (ppm)	Air entrained (percent)
0.08	533	267	0	4.6
.12	600	300	300	3.5
.12	750	375	75	2.8



TABLE IV.- EFFECT OF COMMERCIAL GULF AGENT

Automotive oil (percent)	Defoaming agent (ppm)	Oil	Air in foam (percent)
100	500	Automotive	3.6
10	50	90-percent Aeroshell	6.5
1	5	99-percent Aeroshell	20.8



TABLE V.- ADMIXTURES OF GULF AGENT WITH AEROSOL OT AND/OR GLYCEROL

Gulf agent (ppm)	Aerosol OT (ppm)	Glycerol (ppm)	Air entrained (percent)
500	0	0	3.6
500	100	0	3.9
500	0	100	3.8
5	0	0	20.8
5	100	0	36.1
5	0	100	33.4
5	1	0	29.7
5	0	1	27.8
5	50	100	11.0
500	50	100	4.7
5	.5	1	29.0

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TABLE VI.- RESULTS AT 100° C WITH AEROSOL OT
AND GLYCEROL IN AEROSHELL 120

Concentration (percent)	Colloid mill (qualitative)	Average life of gas in foam (min)
0 (blank)		2.0
0.01 glycerol .01 Aerosol OT	Foam partly removed	1.1
.03 glycerol .01 Aerosol OT	Foam partly removed	1.6
.09 glycerol .03 Aerosol OT	No foam	Less than 0.1
.1 glycerol .1 Aerosol OT	No foam	.1

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