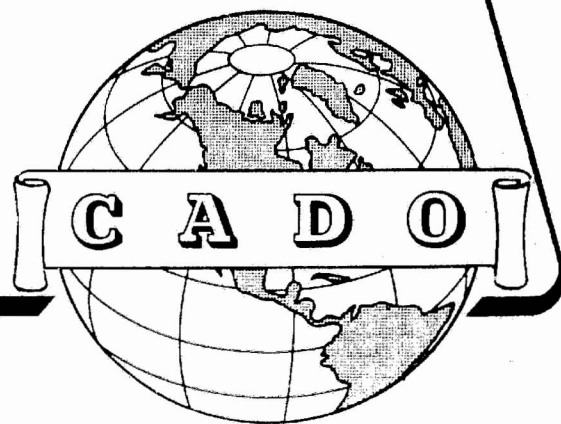


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TECHNICAL NOTE

No. 1842

CONTROL OF FOAMING BY ADDING KNOWN

MIXTURES OF PURE CHEMICALS

By J. W. McBain, Sydney Ross, A. P. Brady, and R. B. Dean

Stanford University



Washington

April 1949

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE NO. 1842

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SUMMARY

Different methods of testing and selection were used to investigate the problem of obtaining satisfactory mixtures of pure chemicals capable of inhibiting both the foaming volume and the foam stability of aeronautical lubricating oil. The method of testing foam volume at room temperature, the bubbling method at high temperatures (100° and 140° C, 212° and 284° F, respectively), and the beating and evacuation method were used.

Thirteen substitutes for glycerol and twenty-seven substitutes for Aerosol OT were tested for defoaming ability at 140° C (284° F) on Aeroshell 120 oil, using a porous ball bubbler. All defoaming emulsions were run to exhaustion of the effect and their durations as antifoam agents recorded. In a ratio of 4 parts glycerol (or substitute) to 1 part Aerosol OT (or substitute) at total concentrations of 1000 to 1500 parts per million, the best of these emulsions completely inhibited foam formation. The best combination was sorbitol and Aerosol OT, 800 and 200 parts per million, respectively, which is an excellent defoamer for 4 hours but leaves a sticky residue in the meter. Glycerol evaporates in 7 minutes at 140° C and in 30 minutes at 100° C leaving no residue. Tests at room temperature have also been conducted and have been of use in suggesting possible substitutions.

INTRODUCTION

It has been shown that mixtures of glycerol and Aerosol OT (dioctyl sodium sulfosuccinate), which are antifoaming agents for aeronautical lubricating oil, are completely effective until the gradual evaporation of the glycerol results in its disappearance from the system. Even in a Lauson engine test, however, lasting 24 hours at 212° F, such a mixture still retained much of its antifoaming property without any deleterious effects on the engine. While the mixture lasts it is more effective than the antifoaming agent now in widespread use because this agent is customarily present in concentrations so low (5 ppm) that the powerful effect of which it is capable is not fully developed. The agent should be used in concentrations of 30 to 50 parts per million and up to 10 times

these amounts in the presence of other additives. Thirty parts per million of this agent remains stable for $1\frac{1}{2}$ hours in laboratory tests at 140° C.

Initial exploratory work was conducted at room temperature. As a result of this work, it was found that many chemicals can be substituted for glycerol, Aerosol OT, or lead Aerosol OT to produce effective mixtures.

In most cases, however, higher temperatures resulted in the loss of one of the necessary constituents of the antifoaming mixture. For example, using a porous ball as bubbler, the glycerol - Aerosol-OT mixtures are effective for only 30 minutes at 100° C; a continuous stream of air through the fluid causes gradual evaporation and loss of the glycerol from the system. Inasmuch as the present trend of engine design is toward the use of higher oil temperatures, a survey of defoaming mixtures at 140° C (284° F) was undertaken. While 140° C is above any probable oil thermostat temperature, the oil is often locally exposed to higher temperatures in the engine.

Preliminary investigations showed that many organic liquids, which in conjunction with Aerosol OT are good defoamers at room temperature, are quite ineffective at higher temperatures. Compounds having high vapor pressures, such as the cellosolves and carbitols, evaporate in the stream of air from the bubbler. The solubility of organic liquids in oils also increases with temperature so that an emulsion at room temperature could form a homogeneous solution at 100° C. It is probable that emulsion droplets are indispensable for defoaming agents of the type herein discussed; hence the reversible inactivation of some of these compounds at high temperatures is readily explained on this basis. The possible substitutes for glycerol are, therefore, presumably limited to liquids insoluble in paraffin oils at 100° to 140° C and less volatile than glycerol.

A list of liquids insoluble in paraffin oils has been published (reference 1). This list contains, besides glycerol and ethylene oxide derivatives, polyamino, polyhydroxyl, and polynitryl aromatic compounds all of which are notoriously unstable at high temperatures in the presence of air. Also mentioned are dicarboxylic acids. Among the higher homologues of glycerol are xylitol and sorbitol, having 5 and 6 carbon atoms, respectively, and equal numbers of hydroxyl groups. Sorbitol is commercially available by the reduction of glucose, whereas xylitol is potentially available as a byproduct of oat hulls.

All the data herein reported are of an exploratory and qualitative nature and further development of this subject will advisedly remain largely of this character for some time to come. Quantitative treatment to discover optimum concentrations is desirable only when compositions of the most effective nature have been ascertained.

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

TEST METHODS

In the beating method, an electric kitchen mixer was used at room temperatures, which were recorded as 24° to 27° C. The specifications of the method have been investigated and described in reference 2. In one series of experiments, conducted at a low temperature, the apparatus had to be modified in order to permit the packing of ice or solid carbon dioxide around the foam vessel. In this case a run with Aeroshell 120 alone had to be made for comparison and calibration.

The beating and evacuation method has been fully described in reference 3. This method was used for room-temperature investigation only and affords only qualitative results.

A Brady porous ball bubbler was used in a 300-cubic-centimeter graduated cylinder jacketed with the condensing vapors of commercial xylenes ($140^{\circ} \pm 1^{\circ}$ C). Air was first blown through water which was heated so that a thermometer in the spray trap at the top of the meter read 56° C. At this temperature, saturated air contains water vapor at a pressure of 124 millimeters of mercury. This is roughly the water content of blow-by gases in the crankcase and corresponds to a relative humidity of 4.6 percent at 149° C or 16 percent at 100° C. In a few runs with sorbitol and xylitol mixtures with Aerosol OT the air that was used was dry. There was no significant difference in the life of the defoaming agent and therefore the use of moist instead of dry air is probably unnecessary in subsequent high-temperature foam studies.

The emulsions tested are classified either as defoamers or as ineffective. The emulsions which prevent a 50-percent increase of volume for 50 seconds or more at high rates of air flow are listed as defoamers. There are virtually no borderline cases; most emulsions which are not defoamers stabilize the foam to some extent or have no effect. The natural foaming tendency of aeronautical oil produces more than 600 percent of the initial volume under these conditions at 140° C (500 percent at 100° C).

RESULTS

Beating Method

The beating method was employed to test mixtures generally similar in nature to the effective Aerosol-OT - glycerol mixture. Table I gives quantitative data from these tests. Aeroshell 120 is the oil medium

used throughout the investigation; without any additive it entrains 51.4 percent of air by volume. The beating test was further employed to test the effect of a change in viscosity (by changing temperature), the effect of 10-percent additions of liquids possibly employed as coolant in the engine, and the effect of adding 30 percent of fuel to the oil. These results are given in tables II, III, and IV, respectively. No data at 100° C could be obtained on these systems because all the gasoline evaporated before the sample reached the test temperature. At room temperature the viscosity is reduced to one-tenth its former value but the actual foaming value is reduced to one-fifth or less by one addition of 30 percent gasoline. The presence of tetraethyl lead in the fuel aids further in reducing the foam volume at 27° C. (See table V.)

Qualitative Search at Room Temperature

A qualitative search for the general type of material suitable for compounding foam inhibitors for aircraft lubricating oils was conducted at room temperature by the beating and evacuation method. Since a mixture of the lead salt of Aerosol OT and glycerol is one of the more effective antifoaming mixtures, in this preliminary survey most of the experiments were of two types: (1) A test of mixtures of different substances with lead Aerosol OT (table VI) and (2) a test of mixtures of different substances with glycerol (table VII). Because of the qualitative nature of the experiments, the results are classified only into antifoam and no effect.

Sorbitol and xylitol form excellent defoaming emulsions with one-quarter their weight of Aerosol OT used at total concentrations of 0.1 to 0.2 percent. They remain good defoamers for 4 hours at 100° C when tested in a bubbler-type foam meter. Table VIII lists other organic substances which were used with Aerosol OT under the same conditions; they are classified as defoamers or ineffective. All the organic liquids used with effective detergents wet the walls of the foam meter. Sorbitol or xylitol form a deposit on the walls of the meter which probably accounts for the ultimate loss of defoaming power. If this deposit forms in an engine, it may rule out these defoaming systems for practical use. Glycerol apparently does not have this undesired property. The chemical compound erythritol, intermediate between glycerol and xylitol, is now under examination.

A number of detergents were tested in an attempt to find a substitute for Aerosol OT but nearly all are ineffective. Table IX shows the detergents which do not form defoaming compounds with sorbitol and also lists the detergents which are effective as defoamers with sorbitol. This set includes, besides Aerosol OT, some of the tergitols which have a polar sulfate radical in the middle of a branched chain and a few phosphoric acid esters having two or more alkyl groups. All the effective detergents are "two tailed." There is at present no explanation why only two-tailed detergents are effective at high temperatures. Some earlier results

showed that a few straight-chain detergents also form antifoaming compounds when used with glycerol at room temperature. The manner in which the mixture is compounded may be understood from the following typical recipe: Sorbitol, 0.8 gram; Aerosol OT, 0.2 gram; water, 1 gram (boils off in hot oil); Aeroshell 120, 19 grams. This mixture is used at concentrations of 1, 2, and 3 percent in Aeroshell 120 at 140° C.

ANALYSIS AND DISCUSSION

Preliminary reports of engine tests conducted on Aerosol OT - glycerol mixtures indicate that when these mixtures are added to lubricating oil in an engine they do not adversely affect any of the necessary qualities of the lubricant. These mixtures even at high temperatures are still effective in materially reducing the foaming value and stability of the oil after use in a test engine. It is therefore probable that the laboratory tests herein reported are more severe and require more qualifications than will be found necessary in actual operation. In the Stanford University laboratory, work has been continued to find substitutes for the constituents of the mixture or to improve it by addition of further constituents so that it will successfully pass the most stringent laboratory test. The bubbling of air through the oil at 140° C causes evaporation of glycerol from the system within 7 minutes. Substitution of the glycerol by sorbitol or erythritol results in a longer period of effectiveness. The best mixture and its optimum concentrations are yet to be definitely established. Meanwhile a large and growing list of substitutes is provided.

The basis for the discovery of substitutes still lacks complete theoretical treatment. It seems clear, however, that hydroxyl groups in the molecule of the liquid dispersed in the oil are greatly effective and even more important than a long carbon chain. Water was the first compound found to activate numerous defoamers until it evaporated. Ethyl alcohol has been found to be effective with Aerosol OT, although its high volatility makes it obviously unsuitable. The larger molecules are more desirable from the point of view of volatility. With large molecules a greater number of hydroxyl groups in the molecule becomes necessary. Substances such as glycerol, sorbitol, and erythritol fulfill these requirements and are more effective. The search for additional compounds has been conducted along the lines thus suggested.

CONCLUDING REMARKS

From different methods of testing, it was found that oils can be defoamed by emulsions stabilized by suitable detergents, among which Aerosol OT is outstanding. The requirements of oil insolubility, low volatility, and low reactivity virtually limited the choice of liquids to the higher polyhydric alcohols. Of these liquids, sorbitol and xylitol

defoam for the longest time. Glycerol evaporates too rapidly in a bubbler foam meter but may be acceptable in actual engine performance.

Stanford University

Stanford University, Calif., January 8, 1945

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2. McBain, J. W., and Ross, Sydney: Quantitative Study of Variations in Concentration of Glycerol and Aerosol OT on Foaming Volume of Oil at Room Temperature. NACA TN No. 1841, 1949.
3. 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.

TABLE I.- RESULTS OF BEATING TEST AT ROOM TEMPERATURE FOR
MIXTURES OF KNOWN CHEMICALS ADDED TO AEROSHELL 120

Constituent A	Concentration of A (ppm)	Constituent B	Concentration of B (ppm)	Air en- trained (percent)
Sodium palmitate	130	Ethylene glycol	106	49.2
Triethanolamine oleate	400	-----do-----	80	48.3
Triethanolamine oleate	400	Glycerol	80	39.3
Morpeloil 455	400	-----do-----	80	50.8
Alronol 100	400	-----do-----	80	34.2
Nacconal NRSF	400	-----do-----	80	49.6
Sodium lauryl sulfonate	300	-----do-----	90	49.6
Sapamine MS	400	-----do-----	80	52.1
Lauryl sulfonic acid	400	-----do-----	80	49.8
Sodium heptadecyl sulfate	400	-----do-----	80	7.6
Sodium octyl sulfate	400	-----do-----	80	46.8
-----	----	Xylidines	10,000	51.5
Aerosol OT	2000	-----do-----	8,000	47.0
Aerosol OT	20	-----do-----	80	51.1
-----	----	-----do-----	10,000	51.5
Aerosol OT	1000	Erythritol	1,600	5.6
Stearic acid	500	-----	-----	50.4
Stearic acid	1000	-----	-----	50.4
Stearic acid	2500	-----	-----	49.4

TABLE II.- ACTUAL FROTHING VOLUMES OF AEROSHELL 120
AND McKESSON'S HYDROL AT COMPARABLE VISCOSITIES

Sample	Temperature (°C)	Viscosity (centistoke)	Air entrained (percent)
McKesson's Hydrol	27	37	6.1
McKesson's Hydrol	-6	603	9.7
Aeroshell 120	27	603	^a 47.0

^aDifference between this value and customary value of 51.4 is due to difference in design of apparatus to make it suitable for use at low temperature.

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TABLE III.- ACTUAL FROTHING VOLUMES OF AEROSHELL 120
IN THE PRESENCE OF COOLANT LIQUIDS¹

Sample	Air entrained (percent)
Ethylene glycol plus 30 percent water	0
Aeroshell 120 plus 10 percent ethylene glycol	39.8
Aeroshell 120 plus 10 percent propylene glycol	40.4
Aeroshell 120 plus 10 percent glycol	39.0

¹These substances when present in oils act as moderate reducers of the actual foaming volume.

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TABLE IV.- EFFECT OF FUELS ON ACTUAL FOAMING VOLUME AT 27° C

Sample	Viscosity (centistoke)	Air entrained (percent)
Aeroshell 120	603	51.5
Aeroshell 120 plus 30 percent 100-octane gasoline	62	10.9
Aeroshell 120 plus 30 percent 100-octane gasoline plus 4 cc TEL per gallon	63	5.7

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TABLE V.- EFFECT OF ADDITIVES ON OILS ALONE AND ON OILS
CONTAINING 30 PERCENT FUEL AT 27° C

Additive	Ratio	Concen- tration (percent)	Fuel	Viscosity (centistoke)	Air entrained (percent)
Triton NE plus Aerosol OT	4:1	0.07	No fuel	603	6.6
Triton NE plus Aerosol OT	4:1	.05	30 percent 100-octane gasoline	61	0
Triton NE plus Aerosol OT	4:1	.05	30 percent 100-octane gasoline con- taining lead	61	.7
Sorbitol plus Aerosol OT	1:1	.10	No fuel	603	9.4
Sorbitol plus Aerosol OT	1:1	.07	30 percent 100-octane gasoline	61	1.8
Wyandotte's Foamicide L		.10	No fuel	603	51.1
None			No fuel	603	51.5

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TABLE VI.- LEAD AEROSOL OT WITH DIFFERENT SUBSTANCES
IN AEROSHELL 120 AT ROOM TEMPERATURE

Additive	Effect	Additive	Effect
Glycerol	Antifoam	Tween 81	No effect
Glycol	-- do --	Triton NE	Do.
Diglycol	-- do --	Polyglycerol	Do.
Butyl Cellosolve	-- do --	Nitropropane	Do.
Butyl carbitol	-- do --	Chlornitropropane	Do.
Trigamine	-- do --		
Tween 20	-- do --		
Triethanolamine	-- do --		



TABLE VII.- GLYCEROL WITH DIFFERENT SUBSTANCES
IN AEROSHELL 120 AT ROOM TEMPERATURE

Additive	Effect	Additive	Effect
Lead Aerosol OT	Antifoam	Lauryl sulfonic acid	No effect
Calcium Aerosol OT	-- do --	Sodium lauryl sulfonate	Do.
Sodium Aerosol OT	-- do --	Ammonium stearate	Do.
Sodium Aerosol MA	-- do --	Catol 607	Do.
Sodium Aerosol IB	-- do --	Cetyl pyridinium chloride	Do.
Diethyl laurylamido phosphate	-- do --	MP-191	Do.
Octyl tripolyphosphate	-- do --	Avirol AH Extra	Do.
Gardinol WA	-- do --	Sulfonated castor oil	Do.
Sodium lauryl sulfate	-- do --		

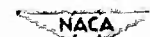


TABLE VIII.- AEROSOL OT WITH DIFFERENT SUBSTANCES
IN AEROSHELL 120 AT 140° C

Defoamers		Ineffective
Additive	Effect	Additive
Sorbitol (6)	Excellent, 1 to 4 hr	Pentaerythritol
Xylitol ¹	Excellent, 1 to 2 hr	Cerbowax 400 (9)
Glycerol	Excellent, 6 to 7 min	Polyvinyl alcohol
Nacconol NRSF	Excellent, 3 min	Triton NE (33)
Sodium lactate	Excellent, 3 min	Sebacic acid
		Glucose
		Sodium gluconate
		Tween 20 (6)
		Phosphoric acid (used with butyl tripolyphosphate)

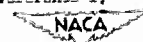
¹Xylitol supplied by Western Regional Laboratories of the U. S. Dept. Agriculture. Source of other chemicals indicated by code number (reference 1, pp. 65-68).



TABLE IX.- SORBITOL WITH DIFFERENT SUBSTANCES¹
IN AEROSHELL AT 140° C

Defoamers		Ineffective	
Additive	Effect	Additive	Second agent
Aerosol OT (4)	Excellent, 1 to 4 hr	Sodium oleate	Emulsol 607 (17)
Phosphorated octyl- amine (42)	Excellent for 90 min	Aluminum oleate	Penatrol 60 (7)
Tergitol Penetrant 4 (9)	Excellent for 75 min	Sodium naphthenate	Albranol (2)
Tergitol Penetrant 7 (9)	Excellent for 30 min	Magnesium naphthenate	Span 20, 40 (6)
Tergitol Penetrant 08 (9)	Excellent for 1 to 2 min	Turkey Red Oil A	Tween 20, 60, 81, 85 (6)
Diethyl lauryl- amidophosphate (42)	Excellent for 30 sec	Sodium lignin sulfonate	Aciterge OL (13)
Octyl tripoly- phosphate (42)	Excellent for 30 sec	Santomine No. 3 (28) (sodium arylal- kyl sulfonate)	Aero Brand Anti-Foam (4)
		Aerosol 05 (4) (alkyl naphtha- lene sulfonate)	Aerosol 22 (4)
			Capryl laurylamine tripolyphosphate (42)

¹Source of chemicals indicated by code number in parentheses (for key see reference 1, pp. 65-68).



Lubrication, Chemistry

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Control of Foaming by Adding Known Mixtures of
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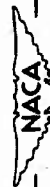
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(Abstract on Reverse Side)

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