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POLYAMIDE ANTIFOAMS. I

Relation Between Chemical Constitution and Effectiveness

ARTHUR L. JACOBY

National Aluminate Corporation, Chicago, Illinois

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Recent research in the problem of foaming in steam boilers has resulted in the development of several types of new chemical compounds possessing unusual merit as antifoams. A large group of such compounds (2, 3, 4, 5) are broadly classed as polyamides. In testing a large number of polyamides as possible boiler antifoams, several interesting relationships were found to exist between chemical constitution and antifoam activity. These relationships are significant when examined in the light of a recently proposed theory of antifoam action (6), and tend further to support this theory.

USE OF ANTIFOAMS

While proper water treatment for softening, clarification, coagulation, and scale-prevention will do much to improve foaming conditions in boiler waters, the benefits of such treatment can frequently be greatly extended by the additional use of an antifoam agent. In the past many substances have been claimed to exert an antifoaming effect in steam boilers and a few, notably castor oil, have been rather widely used. These earlier materials have suffered, however, from several disadvantages, the greatest being their instability under the conditions of alkalinity and temperature encountered in the boiler and their relatively low order of effectiveness. The use of certain polyamides as antifoams has resulted in the solution of many difficult foaming problems and has permitted the concentration of permissible dissolved solids in the boiler water to be increased two- to five-fold, and even more. Such results were unknown with castor oil. Moreover, these polyamide antifoams are effective in extremely low dosages, sometimes of only a few parts per million, or less, in the feed water.

LABORATORY TESTING

The studies reported here were undertaken as a part of a program of investigating the fundamental chemical and physical factors affecting the efficiency of boiler antifoams. The method employed for evaluating the compounds as antifoams has been described elsewhere (6). For the tests reported herein, a feed water was used having the following composition:

Calcium hardness (as $CaCO_3$)	9.0 grains/gallon
Magnesium hardness (as $CaCO_3$)	9.0 grains/gallon
Alkalinity (methyl orange) (as $CaCO_3$)	42.5 grains/gallon
Sodium chloride (as NaCl)	5.0 grains/gallon
Sodium sulfate (as Na_2SO_4)	42.0 grains/gallon
Tannin extract, dry	2.0 grains/gallon

The material to be tested as an antifoam was added as a solution in dioxane of 1.0 mg. of the material per 1.0 ml. of solution. To each 5 gallons of the feed water was added 4.9 ml. of the dioxane solution, resulting in a concentration of antifoam in the feed water of 0.256 p.p.m. (0.015 grain/gallon).

Tests upon the same antifoam by the above procedure are reproducible within a range of approximately ±25 grains/gallon dissolved solids in the boiler water at the time of carryover, when working in the range reported.

PREPARATION OF COMPOUNDS

Since most of the compounds tested and discussed have not previously been described in the literature, their preparation and properties are briefly given below (see table 1).

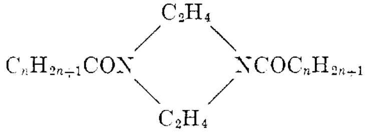
Diacylated piperazines: In each case, the diacylated piperazine was prepared by mixing together one molecular portion of piperazine or its hexahydrate and two molecular portions of the appropriate fatty acid in a 50-ml. flask. The flask was heated in an oil bath and the mixture stirred at a temperature slightly above 100°C. until any tendency for frothing had disappeared, after which it was stirred for 3 hr. at a bath temperature of 150–160°C. The product, which was generally of the nature of a waxy substance, was then recrystallized, usually from methanol or acetone.

N-Octadecylerucamide: This compound was made in an analogous manner from theoretical proportions of erucic acid and *n*-octadecylamine and was recrystallized from a mixture of equal volumes of acetone and low-boiling petroleum ether. Melting point, 70°C. Calculated for $C_{40}H_{79}ON$: N = 2.38 per cent; found, N = 2.36 and 2.38 per cent.

N,N'-Dihexadecylsuccinamide: To 48.2 g. (0.20 mole) of stirred, molten *n*-hexadecylamine at 90–100°C. was added 7.75 g. (0.05 mole) of succinyl chloride fairly rapidly. The temperature was then brought up to 150°C. over a period of 30 min. The warm liquid reaction product was then poured into a mixture of about 400 ml. benzene and 200 ml. ether, treated with solid potassium hydroxide to remove hydrogen chloride, and the filtered solution freed of solvent by evaporation to leave a waxy solid. Recrystallization from a mixture of methanol and ethanol gave a colorless product, melting at 129–130.5°C. Calculated for $C_{36}H_{72}O_2N_2$: N = 4.97 per cent; found, N = 5.10 and 5.08 per cent.

TABLE 1

Melting points and analyses of the diacylated piperazines



n	COMPOUND	FORMULA	MELTING POINT	ANALYSIS FOR NITROGEN	
				Calculated	Found
			°C.	*per cent*	*per cent*
7	Dioctanoylpiperazine	$C_{20}H_{38}O_2N_2$	166	7.73	7.79; 7.83
11	Didodecanoylpiperazine	$C_{28}H_{54}O_2N_2$	133–34	6.24	6.35; 6.19
13	Ditetradecanoylpiperazine	$C_{32}H_{62}O_2N_2$	75	5.53	5.55; 5.53
15	Dihexadecanoylpiperazine	$C_{36}H_{70}O_2N_2$	79.5–80	4.98	5.01; 5.05
17	Dioctadecanoylpiperazine	$C_{40}H_{78}O_2N_2$	83–83.5	4.53	4.42; 4.43

N,N'-Dioctadecylsebacamide: A mixture of 24.2 g. (0.09 mole) of *n*-octadecylamine and 8.1 g. (0.04 mole) of sebacic acid was placed in a 50-ml. flask immersed in an oil bath and stirred for 3 hr. at a bath temperature of 150–160°C. The product was recrystallized from 2-propanol, using decolorizing carbon. Melting point, 132–133°C. Calculated for $C_{46}H_{92}O_2N_2$: N = 3.97 per cent; found, N = 4.06 and 4.03 per cent.

TEST RESULTS

Laboratory boiler tests were carried out, as described above, on several materials, each employed at a dosage of 0.256 p.p.m. in the feed water entering the boiler. For purposes of comparison, runs were also made in which no material was added as an antifoam (but the usual amount of dioxane was included in the feed water), and in which castor oil was added. Results are shown in table 2. The higher the dissolved solids value shown, the more effective is the material as an antifoam.

INTERPRETATION OF RESULTS

The results show, first, the remarkable superiority of certain of the polyamides as boiler antifoams over the previously used castor oil. The conditions of the test were purposely made rather severe so as not to prolong unduly a test in which one of the better antifoams was being evaluated. The substantial differences found between the action of castor oil and of several of the diamides are substantiated by field experience.

Secondly, the results tend to strengthen the theory of antifoam action recently suggested by Jacoby and Thompson (6). Briefly stated, the mechanism of the rupture of double-faced liquid films, e.g., of bubble films, consists of the gradual thinning of these films, due to drainage of liquid, until the film reaches a critical minimum thickness and is destroyed (7). In the presence of an adsorbed layer of surface-active insoluble material, the collapse of a foam bubble may be accompanied by a syneresis (8) or formation in the adsorption layers of dehydrated aggregates of the surface-active material. It has been observed that certain monolayers, although they may actually stabilize the bubble film while they are in the liquid state, lose this ability at once when the solid (brittle) state is attained (8). This indicates that one of the conditions for stabilization is the great mobility of the molecules of the adsorption layers, and if this mobility is lost by attainment of the solid state, the adsorption layers may contribute to the rupture of the bubble film. It is likely that the syneresis described above results essentially in the formation of patches of monolayer in the brittle state which are incapable of redispersion at a rate equal to or greater than the velocity of destruction of the bubble film.

TABLE 2

Test results on antifoams

COMPOUND	BOILER WATER DISSOLVED SOLIDS AT CARRYOVER	MOLECULAR WEIGHT
	grains/gallon	
None (dioxane only)	170	
Octadecanamide	166	283
Dioctanoylpiperazine	189	362
Didodecanoylpiperazine	184	450
Ditetradecanoylpiperazine	218	506
Dihexadecanoylpiperazine	378	562
Dioctadecanoylpiperazine	475	618
N-Octadecylerucamide	201	589
N,*N*′-Dihexadecylsuccinamide	563	564
N,*N*′-Dioctadecylsebacamide	978	704
Castor oil	186	

Table 2 shows that the monoamide, octadecanamide, showed no antifoam action, and that a substantial increase in the molecular weight brought about by the introduction of a second long fatty chain, as in *N*-octadecylerucamide, imparted but slight antifoam action. However, the introduction into the molecule of a second amide group resulted in antifoam action if the molecular weight was sufficient. Thus, the diamide formed by the diacylation of piperazine with a fatty acid of fourteen or more carbon atoms showed pronounced antifoam action. The theory of antifoam action referred to above suggests that hydrogen bonding promotes antifoam action by enhancing the syneretic effect and creating a greater tendency for the monolayer to reach the solid or brittle state, as shown by Alexander (1). A consideration of the hydrogen bonding possible in the case of the monoamides as contrasted to that possible with the diamides will reveal that the extensive cross-linking of the latter should favor the effects believed responsible for antifoam action.

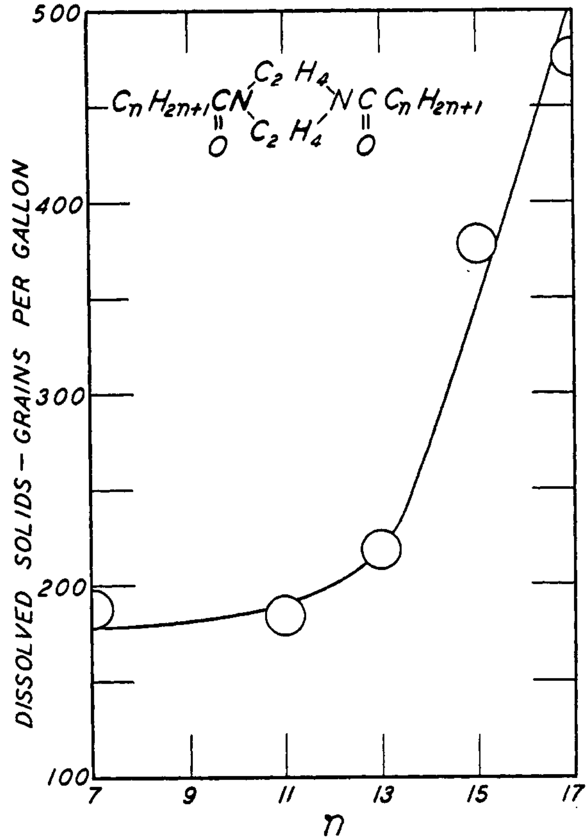


FIG. 1. Increasing antifoam effectiveness of diacylated piperazines with increasing molecular weight.

The superiority of the diamides over the monoamides cannot be ascribed merely to the fact that many of the better diamides are of relatively high molecular weight. While there appears to be a certain minimum requirement as to molecular weight in order that the diacylated piperazines act as antifoams in a boiler, a comparison of the molecular weights given in table 2 will show that several of the diamides tested were of lower molecular weight than *N*-octadecylerucamide, an almost ineffective, high-molecular-weight monoamide, yet they were effective antifoams. That an increase in molecular weight causes the diacylated piperazines to become increasingly effective is well shown by reference to figure 1. Table 2 will show that this same tendency holds in the case of *N*,*N'*-dihexadecylsuccinamide and *N*,*N'*-dioctadecylsebacamide, although in the case of these two compounds both the acid and the amine were increased in size in going from the former to the latter. The increase in effectiveness with increasing length of the fatty chains is probably due to an increase in the van der Waals cohesive forces whereby solidification is brought about more readily (1).

That chemical constitution, as well as molecular weight, is important is further demonstrated by a comparison of the effectiveness of dihexadecanoylpiperazine and *N*,*N'*-dihexadecylsuccinamide. The molecular weight of the latter is only two more than that of the former, yet the succinamide is considerably more effective as an antifoam. A possible explanation of this in the light of the theory under discussion is that the piperazine derivative can only be linked together by hydrogen bonding through the agency of another kind of molecule, such as water. In the case of the succinamide derivative, however, this is not the case. Each amide group in the succinamide bears a hydrogen whereby hydrogen bonding may be effected to the carbonyl oxygen of a neighboring molecule without the necessity for some intermediary.

SUMMARY

Antifoam tests were conducted in an experimental boiler on a series of piperazines diacylated by fatty acids, and on several other amides and castor oil. Of the diamides tested, those of sufficient molecular weight were more effective than castor oil or either of two monoamides. The effectiveness of the diacylated piperazines was shown to increase with increasing length of the fatty chains. Two diamides of almost identical molecular weight, one a diacylated piperazine and the other a succinamide derivative, differed widely in effectiveness. The results were interpreted in terms of a recently formulated theory of antifoam action.

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