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ORGANIC ANTI-FOAMING AGENTS

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Within the last few years the undesirable foaming of liquids in many instances has been controlled by the employment of a variety of organic anti-foaming agents of diverse types. Ross (1) in a review has listed higher alcohols, fatty acids and their esters, fatty acid amides, ethers, organic phosphates, metallic soaps, and silicone resins. The choice and utility of these materials usually must be determined experimentally because seemingly minor variations in their compositions greatly modify their properties. So far as foam inhibition in steam generators is concerned, it has been shown (2, 3) that alkylene polyamides possessing both hydrophilic and hydrophobic groups are the most stable and useful materials.

This research concerns the preparation of a number of related nitrogenous organic compounds for testing as anti-foaming agents in steam generating equipment. Observation of the results of the tests recorded in Table I suggests that effectiveness is a rare characteristic and is possibly dependent on polar and nonpolar groups being in proper balance as proposed by Gunderson and Denman (2). Anti-foaming tests were run on synthetic boiler water (2) and were made in the laboratories of the Dearborn Chemical Company. In the table is shown the time in minutes during which each material prevented the development of a standard foam.

The first series of compounds contains symmetrical diamides of hexamethylenediamine prepared by the reaction of hexamethylene diisocyanate with two molecules of the respective acids as expressed by the following equation.

$$OCN(CH_2)_6NCO + 2\,RCOOH \rightarrow 2\,CO_2 + RCONH(CH_2)_6NHCOR$$

All are totally or relatively ineffective except the amides of palmitic and stearic acids and, to a lesser extent, behenic acid.

A series of diurethans and of dicarbamido derivatives were prepared from hexamethylene diisocyanate with alcohols and amines, respectively.

$$OCN(CH_2)_6NCO + 2\,ROH \rightarrow ROCONH(CH_2)_6NHCOOR$$

$$OCN(CH_2)_6NCO + 2\,RNH_2 \rightarrow RNHCONH(CH_2)_6NHCONHR$$

Moderate effectiveness as anti-foaming agents was observed for the diurethans of the longer alcohols. The urea derivatives were ineffective, possibly due in part to their very low solubility in water.

Evaluation of a brief series of diamides formed by the reaction of octadecyl isocyanate with selected dibasic acids shows that it is preferable to have the two amide groups separated by about six carbon atoms. The most satisfactory material in this series, N,N′-dioctadecyladipamide, is very similar to the best product in the first diamide series, N,N′-distearoylhexamethylenediamine. The

TABLE I

ORGANIC ANTI-FOAMING AGENTS

Reagent	Product	Recryst. Solvent[a]	M.P., °C.	Lit. M.P., °C.	Ref.	Anti-foam, Min.	Formula	N	
								Calc'd	Found
A. HEXAMETHYLENEDIAMINE + 2 RCOOH									
Acetic acid	N,N'-Diacetylhexamethylenediamine	E	126–127	126	(4)	0	$C_{10}H_{20}N_2O_2$	14.00	—
Propionic acid	N,N'-Dipropionylhexamethylenediamine	E-A	128–130	—		0	$C_{12}H_{24}N_2O_2$	12.29	12.35
n-Butyric acid	N,N'-Di-*n*-butyrylhexamethylenediamine	E-A	137–139	—		0	$C_{14}H_{28}N_2O_2$	10.94	11.00
Valeric acid	N,N'-Divalerylhexamethylenediamine	E-A	137–138	—		0	$C_{16}H_{32}N_2O_2$	9.87	10.07
Heptylic acid	N,N'-Diheptoylhexamethylenediamine	E-A	141–143	—		0	$C_{20}H_{40}N_2O_2$	8.23	8.36
Caprylic acid	N,N'-Dicaprylylhexamethylenediamine	E-A	144–145	—		0	$C_{22}H_{44}N_2O_2$	7.61	7.52
Pelargonic acid	N,N'-Dipelargonylhexamethylenediamine	E-A	142–143	—		0	$C_{24}H_{48}N_2O_2$	7.07	7.09
Capric acid	N,N'-Dicaprylhexamethylenediamine	E	143–144	—		0	$C_{26}H_{52}N_2O_2$	6.61	6.75
Undecylenic acid	N,N'-Diundecylenylhexamethylenediamine	E-A	133–134	—		0	$C_{28}H_{52}N_2O_2$	6.25	6.68
Lauric acid	N,N'-Dilaurylhexamethylenediamine	E-H	146–147	147	(7)	0	$C_{30}H_{60}N_2O_2$	5.83	5.99
Myristic acid	N,N'-Dimyristylhexamethylenediamine	E-H	146–148	—		0	$C_{34}H_{68}N_2O_2$	5.23	5.27
Palmitic acid	N,N'-Dipalmitylhexamethylenediamine	H	146–147	—		123	$C_{38}H_{76}N_2O_2$	4.73	4.73
Stearic acid	N,N'-Distearylhexamethylenediamine	H	145–146	140	(7)	144	$C_{42}H_{84}N_2O_2$	4.32	4.35
Behenic acid	N,N'-Dibehenylhexamethylenediamine	H	144–145	—		20	$C_{46}H_{92}N_2O_2$	3.97	3.85
Diphenylacetic acid	N,N'-Bis-diphenylacetylhexamethylenediamine	E-A	177–179	—		0	$C_{34}H_{36}N_2O_2$	5.56	6.3
Phenylacetic acid	N,N'-Diphenylacetylhexamethylenediamine	E-A	165–166	—		0	$C_{22}H_{28}N_2O_2$	7.95	7.89
B. HEXAMETHYLENEDIISOCYANATE AND 2 ROH OR 2 RNH_2									
Hexanol-1	Bis-(*n*-hexyl-N-trimethylenecarbamate)	E-B	103–106	—		0	$C_{20}H_{40}N_2O_2$	7.54	7.42
Decanol-1	Bis-(n-decyl-N-trimethylenecarbamate)	E-B	111–112	—		0	$C_{28}H_{56}N_2O_4$	6.03	5.89
Tetradecanol-1	Bis-(tetradecyl-N-trimethylenecarbamate)	H	118–119	—		50	$C_{36}H_{72}N_2O_4$	4.68	4.50
Octadecanol-1	Bis-(octadecyl-N-trimethylenecarbamate)	H	120–121	—		15	$C_{44}H_{88}N_2O_4$	3.95	3.94
n-Octylamine	Bis-(N-octyl-N'-trimethyleneurea)	H	188–189	—		0	$C_{24}H_{50}N_4O_2$	13.14	12.99
n-Octadecylamine	Bis-(N-octadecyl-N'-trimethyleneurea)	H	174–175	—		0	$C_{44}H_{90}N_4O_2$	7.82	7.66

C. Octadecylisocyanate and Acids, Amines, or Alcohols

Adipic acid	N,N′-Dioctadecyladipamide	H	145–146	—		167	$C_{42}H_{84}N_2O_2$	4.32	4.46
Azelaic acid	N,N′-Dioctadecylazelaic amide	H	126–127	—		34	$C_{45}H_{90}N_2O_2$	4.06	4.27
Sebacic acid	N,N′-Dioctadecylsebacamide	H	134–135	—		40	$C_{46}H_{92}N_2O_2$	3.97	4.22
n-Octylamine	N-Octyl-N′-octadecylurea	H	96– 97	—		0	$C_{27}H_{56}N_2O$	6.58	6.20
n-Octadecylamine	N,N′-Dioctadecylurea	H	113–114	106	(8)	0	$C_{37}H_{76}N_2O$	4.96	4.79
Decamethylene glycol	Bis-(pentamethylene-N-octadecylcarbamate)	H	114–115	—		0	$C_{48}H_{96}N_2O_4$	3.66	3.66
Valeric acid	N-Octadecylvaleramide	E	77– 78	77	(5)	0	$C_{23}H_{47}NO$	3.99	—
Caprylic acid	N-Octadecylcaprylamide	E	78– 79	79	(5)	0	$C_{26}H_{53}NO$	3.54	—
Lauric acid	N-Octadecyllauramide	E	82– 84	87	(5)	4	$C_{30}H_{61}NO$	3.09	3.25
Myristic acid	N-Octadecylmyristamide	E	88– 89	89	(5)	0	$C_{32}H_{65}NO$	2.91	—
Stearic acid	N-Octadecylstearamide	E	95– 96	96	(5)	0	$C_{36}H_{73}NO$	2.61	—
Hexanol-1	*n*-Hexyl-N-octadecylcarbamate	E	63– 65	—		0	$C_{25}H_{51}NO_2$	3.53	3.5
Decanol-1	*n*-Decyl-N-octadecylcarbamate	E	71– 73	—		0	$C_{29}H_{59}NO_2$	3.09	3.1
Tetradecanol-1	*n*-Tetradecyl-N-octadecylcarbamate	H	76– 77	—		0	$C_{33}H_{67}NO_2$	2.74	2.79
Octadecanol-1	*n*-Octadecyl-N-octadecylcarbamate	H	84– 86	—		0	$C_{37}H_{75}NO_2$	2.47	2.37

D. N-Acylhexamethylenediamine and Acids or Isocyanates

—	N-Acetyl-N′-laurylhexamethylenediamine	E	131–132	—		0	$C_{20}H_{40}N_2O_2$	8.23	8.14
—	N-Acetyl-N′-stearylhexamethylenediamine	E	135–136	—		0	$C_{26}H_{52}N_2O_2$	6.61	6.4
—	N-Lauryl-N′-stearylhexamethylenediamine	B	137–138	—		57	$C_{36}H_{72}N_2O_2$	5.00	4.5
—	N-Lauryl-N′-phenylcarbamylhexamethylenediamine	E	144–145	145	(6)	0	$C_{25}H_{43}N_3O_2$	10.00	9.98
—	N-Stearyl-N′-phenylcarbamylhexamethylenediamine	B	145–146	—		0	$C_{31}H_{55}N_3O_2$	8.4	8.1
—	N-Stearyl-N′-octadecylcarbamylhexamethylenediamine	B	150–151	—		10	$C_{43}H_{87}N_3O_2$	6.2	6.2

[a] Recrystallization solvents: E-ethanol; A-acetone; H-acetic acid; B-*n*-butyl alcohol.

bifunctional products obtained by the addition of octadecyl isocyanate to hexamethylenediamine and to decamethylene glycol, respectively, were ineffective.

Gunderson and Denman (2) emphasized that di- or poly-functional compounds, especially selected diamides, gave the best results. This conclusion is supported by evaluation of the series of amides, ureas, and urethans formed by the reaction of octadecyl isocyanate with monofunctional acids, amines, and alcohols, respectively. All these products with only one functional group were ineffective as anti-foaming agents.

Gunderson and Denman also called attention to the diamide, possibly N-stearoyl-N′-acetylethylenediamine, formed by the condensation of one mole of ethylenediamine with one mole each of stearic and acetic acids, which diamide proved unsatisfactory as an anti-foaming agent. This material possibly was a complex mixture of N,N′-distearoylethylenediamine, N,N′-diacetylethylenediamine, and N-stearoyl-N′-acetylethylenediamine. To determine more accurately the possible utility of diamides of hexamethylenediamine with two different acyl groups, stearoylhexamethylenediamine and lauroylhexamethylenediamine were converted, respectively, into pure diamides of mixed types. These products are listed last in the table. It will be observed that their effectiveness as anti-foaming agents is very low except in the instance of N-lauroyl-N′-stearoylhexamethylene, which was moderately satisfactory, although to a lesser extent than the best diamide, N,N′-distearoylhexamethylenediamine.

EXPERIMENTAL

Amides from isocyanates. The following preparation serves to illustrate the general procedure for preparing amides from acids and either octadecyl isocyanate or hexamethylene diisocyanate.

Into a dry test tube is placed hexamethylene diisocyanate (1.0 g., 0.0059 mole) and then myristic acid (2.90 g., 0.0127 mole) is added portionwise. The mixture, which initially becomes quite warm, is heated in an oil bath to 150° and then is maintained for 90 min. at this temperature, when carbon dioxide no longer is evolved. The wax-like solid which results on cooling is recrystallized twice from acetic acid to give 2.1 g. of N,N′-dimyristylhexamethylenediamine, m.p. 146–148°.

Ureas and carbamates from isocyanates. In the customary manner, the mixture of amine or alcohol with the isocyanate, with or without inert solvent, reacted spontaneously to give the product which then was recrystallized from a selected solvent.

N-Lauroyl-N′-stearoylhexamethylenediamine. The mixed diamides of known structures were made as illustrated from the pure mono-amides of hexamethylenediamine. N-Stearoylhexamethylenediamine (0.65 g.) is dissolved in dry pyridine (10 cc.) and then warmed briefly with lauroyl chloride (1.0 g.). The product is poured into water, washed thoroughly, and recrystallized from *n*-butyl alcohol; m.p. 137–138°.

N-Stearoyl-N′-octadecylcarbamylhexamethylenediamine. N-stearoylhexamethylenediamine (1.37 g.) in 40 cc. of warm benzene is heated with octadecyl isocyanate (1.27 g.). The mixture is gently boiled to remove about half the solvent. Upon cooling, 1.5 g. of product separates, m.p. 148–151°. Recrystallization from *n*-butyl alcohol-acetic acid gave m.p. 150–151°.

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SUMMARY

1. Several series of diamides, ureas, and urethans were prepared.

2. Only a very few of the compounds, mainly selected long-chain diamides, proved to be effective anti-foaming agents.

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