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The Preparation and Properties of Amines and Cationic Surfactants from Fatty Acids

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Abstract

The general industrial chemical methods of preparation of primary, secondary, and tertiary amines and quaternary ammonium compounds are discussed. The physical properties and uses of the amines and quaternary ammonium compounds are described. Particular attention is paid to corrosion inhibition of steel, to ore flotation of taconite ores, to solvent extraction of uranium ores, and to the use of cationic surfactants as emulsifiers for asphalt and as fabric softeners and antistatic agents. The relationship of chemical structure to performance in the above applications is covered.

Introduction

PRIOR TO WORLD WAR II soap-based products for consumer and industrial use dominated the soap and detergent market and consumed vast quantities of fatty acids and their corresponding triglycerides. In 1947 the synthetic detergent-based Tide was introduced into the American consumer market and made a large-scale impact. By the year 1953 the production of synthetic detergent-based products surpassed that of soap-based products (1.9 billion lbs to 1.6 billion lbs). In 1964 a total of 5.1 billion lbs of production was realized, but only 0.97 billion lbs of this volume were soap-based products (1).

Such a decline in the production of soap-based products has had a significant effect upon the fatty acid market. It is confidently believed however that the fatty acids will remain extremely important compounds in the chemical market and indeed may be facing a resurgence for two reasons. The decline in the sale of soap-based products is probably reaching a plateau. The importance of derivatives of fatty acids is increasing significantly, particularly in new areas of application and technology.

This presentation will be confined to the preparation of nitrogen-based derivatives from fatty acids, particularly 1°, 2°, and 3° amines and quaternary ammonium compounds, and to a brief exploration of their newer uses and applications.

Preparation of Amines

The industrial preparation of fatty amines is accomplished by standard and well-known chemical reactions, as represented below:

1) $RCOOH + NH_3 \rightleftarrows RCOONH_4$

2) $RCOONH_4 \overset{\Delta}{\rightleftarrows} RCONH_2 + H_2O$

3) $RCONH_2 \overset{\Delta}{\rightleftarrows} R{-}CN + H_2O$

4) $R{-}CN + 4\,[H] \underset{cat}{\overset{\Delta}{\rightleftarrows}} R{-}CH_2{-}NH_2$ (1° amine)

5) $2\,R{-}NH_2 \overset{\Delta}{\rightleftarrows} R_2NH + NH_3$ (2° amine)

6) $R_2NH + RNH_2 \rightleftarrows R_3N + NH_3$ (3° amine)

INDEX

TABLE I

Compound	Surface Tension 0.05% Active dispersion (dynes/cm)	Interfacial Tension 0.05% Active dispersion (dynes/cm)
Coco 1° amine hydrohalide salt	24.8	4.0
Coco 1° amine $HC_2H_3O_2$ salt	24.8	5.1
Tallow 1° amine hydrohalide salt	25.2	1.7
Tallow 1° amine $HC_2H_3O_2$ salt	25.4	7.8
Stearyl trimethyl ammonium chloride	38.6	10.2
Ditallow dimethyl ammonium chloride	34.3	1.4
Tricoco methyl ammonium chloride	25.9	1.4

All of the above reactions, of course, are equilibrium reactions and therefore, by suitable control of the reaction conditions, the desired amine will predominate in the resulting product. As an example, in the reduction of the nitrile as shown in Reaction 4), if ammonia is fed with the hydrogen, the formation of primary amine will be greatly favored. Similarly, if only limited quantities of ammonia are introduced into the reaction system, high yields of the secondary amine will result. If no ammonia is introduced during the hydrogenation step or if any ammonia which is formed is removed from the system, the formation of tertiary amine will dominate.

Fatty amines can also be produced from fatty alcohols according to the reaction:

7) $R\text{–}OH + NH_3 \underset{cat}{\rightleftarrows} R\text{–}NH_2 + H_2O$

Again, high yields of 1°, 2°, or 3° amines can be obtained by suitable control of the reaction conditions. The fatty acid is usually the raw material of choice for the production of fatty amines because of the high cost of the fatty alcohol.

As is to be expected from these reactions in the production of 1°, 2°, or 3° amines, the resulting crude product is a mixture of all three types of amines. These crude products are usually of sufficiently high purity that they can be sold and used as "technical" grade amines. If extremely high purity is required, they can be purified by careful distillation.

Diamines of the propylene diamine type are also of increasing interest. They are usually prepared by reacting a suitable primary amine with acrylonitrile, followed by reduction, according to the following reactions:

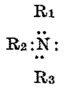
8) $R\text{–}NH_2 + H_2C = CH\text{–}CN \underset{cat}{\rightleftarrows} R\text{–}NH\text{–}CH_2\text{–}CH_2\text{–}CN$

9) $R\text{–}NH\text{–}CH_2\text{–}CH_2\text{–}CN + 4\,[H] \rightleftarrows R\text{–}NH\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}NH_2$

The resulting molecule is, of course, a polyfunctional molecule with 1° and 2° amine reaction sites.

Preparation of Cationic Surfactants

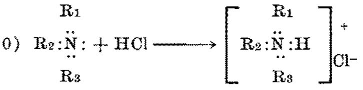
The mono fatty amines may therefore be considered compounds with the general electronic structure,



$$\underset{R_3}{\overset{R_1}{R_2\!:\!\ddot{N}\!:}}$$

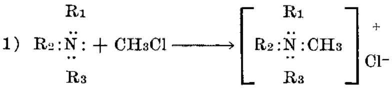
in which R_1 is an alkyl group and R_2 and R_3 may be alkyl groups or hydrogen in any combination. This general structure can be used to represent a 1°, 2°, or 3° amine. The presence of the unshared pair of electrons allows these molecules to undergo two useful reactions: salt formation with acids and exhaustive alkylation with alkylhalides. Typical examples of these reactions are:

10)



$$\underset{R_3}{\overset{R_1}{R_2\!:\!\ddot{N}\!:}} + HCl \longrightarrow \left[\underset{R_3}{\overset{R_1}{R_2\!:\!\ddot{N}\!:\!H}}\right]^+ Cl^-$$

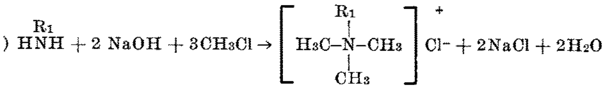
11)



$$\underset{R_3}{\overset{R_1}{R_2\!:\!\ddot{N}\!:}} + CH_3Cl \longrightarrow \left[\underset{R_3}{\overset{R_1}{R_2\!:\!\ddot{N}\!:\!CH_3}}\right]^+ Cl^-$$

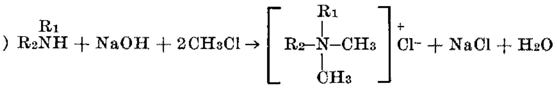
If the amine in reaction 11) is a tertiary amine, the reaction proceeds as represented. If it is a 1° or 2° amine, the reactions are only slightly more complicated, and exhaustive methylation will result according to the following reactions.

12)



$$\overset{R_1}{HNH} + 2\,NaOH + 3CH_3Cl \rightarrow \left[\underset{CH_3}{\overset{R_1}{H_3C\text{–}N\text{–}CH_3}}\right]^+ Cl^- + 2NaCl + 2H_2O$$

13)



$$\overset{R_1}{R_2NH} + NaOH + 2CH_3Cl \rightarrow \left[\underset{CH_3}{\overset{R_1}{R_2\text{–}N\text{–}CH_3}}\right]^+ Cl^- + NaCl + H_2O$$

Commonly the reaction shown in 10) is referred to as amine salt formation, and the one in 11) as quaternization. In truth, both reactions are types of quaternization, and the resulting compounds can properly be called cationic surfactants. Evidence of their surface-active properties is shown in Table I. The salts of amines and hydrochloric and acetic acid are the only salts considered in this paper, and the subject is further confined to quaternary ammonium compounds formed by the exhaustive reaction of amines with methyl chloride.

It can readily be seen from the data in Table I that the quaternary ammonium compounds have a high degree of surface activity in aqueous solution, and this leads to the conclusion that these compounds should potentially be useful detergents and emulsifiers.

Some Uses of Amines

As one carefully considers the use applications of alkyl amines, he becomes somewhat obsessed with the idea that in all, or nearly all, of their uses, the amines are functioning as chemical intermediates. They are converted to new chemical derivatives, such as ethoxylates, propoxylates, amine oxides (in the case of 3° amines), or quaternary ammonium compounds, to name a few, prior to use. When the free amine itself is introduced into a system, it usually reacts with some other reagent present in the system *in situ* so that, again, an amine derivative is the functional compound.

Corrosion Inhibition

The C_{12} to C_{18} acetate salts of primary amines are excellent corrosion-inhibitors for iron and steel and are being used in ever-increasing quantities for this application.

A brief description of the evaluation test used by Ashland Chemical for screening corrosion inhibitors is in order. Essentially, a 5.0% NaCl solution is prepared and saturated with H_2S so that the resulting brine contains 500 ± 50 ppm of H_2S and has a pH of 3–4. Then 800 ml of this solution are transferred to clean, one-liter jars. Mild 1010 carbon steel strips are machined to the dimensions ½-in. × 6-in. × 24 gauge. Each strip therefore has essentially the same surface area and the same weight. One strip is then fastened to the jar cap in a rigid manner. The strip

FIG. 1. Test bottle fully assembled.

is then immersed into the jar, and the cap is tightly sealed onto the jar. The dimensions of the steel strip and the jar are such that, when the cap is in place, one-half of the steel strip is immersed in the H_2S-brine solution, and the other half is exposed to the air above the liquid. The jars are rigidly clamped into an apparatus which rotates at 16 rpm so that, during operation, the upper and lower halves of the test strip are alternately exposed to the air and the brine solution.

Fig. 1 shows a test bottle fully assembled, and Fig. 2 shows the test apparatus also fully assembled and ready for use. In the test, the apparatus is rotated continuously 24 hr per day for 5 days. At the end of this time the test strips, which initially had been thoroughly cleaned, dried, and weighed, are removed. The test strips are thoroughly rinsed, then immersed in an inhibited 15% HCl solution for exactly 60 sec, rinsed, dried, and weighed again. A clean control test strip is also run simultaneously in which no inhibitor is added to the brine-H_2S solution. The weight losses of the test strips and the control strip are then compared, and the percentage protection offered by the corrosion inhibitor is calculated according to the equation

$$\frac{(\text{weight loss of control strip—weight loss of test strip})}{(\text{weight loss of control})} \times 100 = \underset{\text{protection}}{\%}$$

The reproducibility of the test is relatively good and is demonstrated by the data in Table II. Naturally the concentration of the corrosion inhibitor is usually held at the lowest level possible, consistent with good corrosion inhibition, if corrosion inhibition is the only function of the amine in the system. The inhibition characteristics of the amine under evaluation are run at levels of 2, 5, 10, and 25 ppm of amine, based upon the weight of the brine solution. The acetate salt of coco primary amine is used as the standard inhibitor.

Experience has shown that this compound will consistently afford approximately 95% protection to the steel strip at 25 ppm concentration, hence its selection as a standard for comparison. It will also be noted from Table II that, at lower concentrations of amine salt, such as 2 and 5 ppm, the percent protection tends to be erratic. In the range of 10 to 25 ppm, the increase in percent protection is beginning to level off and make a plateau. In general, a compound is considered to be an effective corrosion-inhibitor if a concentration can be found at which 90% protection or higher is achieved by this test.

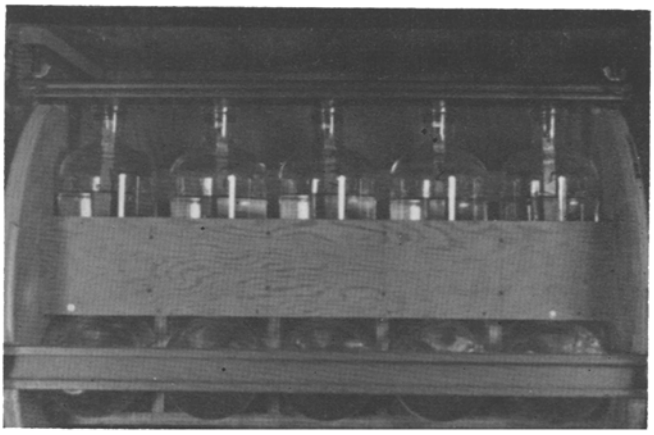


FIG. 2. Test apparatus fully assembled and ready for use.

TABLE II

Evaluation of Corrosion Inhibition of the Acetate Salt of Coco Primary Amine

	% Corrosion Protection			
	2 ppm	5 ppm	10 ppm	25 ppm
Run 1	16.3	79.2	94.2	95.2
Run 2	37.1	81.0	93.4	94.0
Run 3	24.7	27.1	84.7	97.0
Run 4	58.2	81.7	95.0	93.4
Run 5	0.0	57.8	79.3	93.9

The acetate salts of the primary amines are generally used in order to speed the solubility and disperse the amine. Table III shows a performance comparison of the coco primary acetate with that of an oleyl-linoleyl primary amine acetate and two ethoxylated derivatives of oleyl-linoleyl primary amine.

There appears little or no performance difference between the coco and the oleyl-linoleyl primary amines. These data tend to indicate that any C_{12} to C_{18} saturated, straight-chain primary amine acetate salt will be an effective corrosion-inhibitor. The ethoxylated derivatives are not as effective as corrosion inhibitors, probably because they are too water-soluble.

Ore Benefaction

The amines are being used in increasing quantities for the benefaction of ores, either as flotation reagents or as solvent-extraction reagents.

Flotation Reagents. Flotation reagents are used, of course, for froth separation and concentration of a desirable component of an ore or for removing from the froth an undesirable component of the ore.

Most of today's domestic potash production involves a froth flotation process, which uses aliphatic primary

TABLE III

Corrosion Inhibition Comparison Between Coco and Oleyl-Linoleyl Primary Amine Derivatives

Compound	% Corrosion Protection			
	2 ppm	5 ppm	10 ppm	25 ppm
Coco primary amine acetate	16.3	79.2	94.2	95.2
Oleyl-Linoleyl primary amine acetate	27.8	78.3	86.2	95.6
2 Mole ethoxylate of oleyl-linoleyl primary amine 50% neutralized with acetic acid	55.1	77.9	61.9	84.4
10 Mole ethoxylate of oleyl-linoleyl primary amine not neutralized	39.4	73.1	82.1	74.0

TABLE IV
KCl Flotation Test Results

Compound (used as hydrochloride salts)	Use Level (lbs amine hydrochloride per ton of sylvinite ore)	% KCl recovery	% KCl in concentrate
Tech tallow 1° amine	0.15	63.8	94.5
Tech tallow 1° amine	0.25	92.4	90.2
Phenyl stearyl 1° amine	0.15	36.7	87.3
Phenyl stearyl 1° amine	0.25	55.6	85.2

amine salts as flotation agents to beneficiate sylvinite ores. A typical sylvinite ore contains 25 to 30% of KCl (sylvite), 60 to 65% NaCl (halite), and 2 to 8% of other soluble, inorganic salts.

In principle then, the process essentially involves the separation of KCl from NaCl. Primary amine hydrohalides of the coco, tallow, or oleyl-linoleyl types are used with good success. A wide variety of primary amine hydrohalides has been evaluated for this application, but these three types or combinations of them have proved most effective. The technical tallow primary amine is the most economical (2). Atwood has correlated flotation efficiency with unsaturation of the amine and brine temperature (3). In general, the colder the brine, the more unsaturated the amine should be for optimum results; or blends of coco and tallow amine should be used. At high brine temperatures, saturated amines, such as stearyl amine, function best.

Table IV shows an example of the performance of technical tallow primary hydrohalide for this application. Included, merely as a comparison example, is the performance of phenylstearyl amine hydrohalide.

From the data in Table IV it can be readily seen that the technical tallow primary amine at the proper use level is an extremely effective KCl flotation reagent. The performance of the phenylstearyl amine indicates that any structural modification of the amine molecule can adversely affect the performance of the amine as a flotation reagent for this application.

It should be noted also that the aliphatic primary amine salts as KCl collectors are preferred for two reasons. Aliphatic 1° amine salts will effectively concentrate coarse sylvite, hence reducing the amount of crushing and grinding necessary during the preparation of the ore for flotation. Aliphatic 1° amine salts function as effective anti-caking agents in the recovered KCl. If the KCl is recovered by anionic reagents, anti-caking agents must be incorporated into the recovered KCl during some step in the operation whereas, with cationic flotation, the addition of anticaking agents may not be necessary.

The taconite industry is now beginning to use 1° alkyl amines for the removal of silica from magnetically separated taconite iron ore. To be suitable for use in the steel industry today, the ore must contain a minimum of 64% iron and a maximum of 8% silica.

In essence, the crude taconite ore is crushed and ground to the 325-mesh size range, then subjected to magnetic separation. The crude taconite ore will contain 30 to 35% Fe and 50 to 55% SiO_2. After magnetic separation the taconite ore will contain 62 to 65% Fe and 6 to 12% SiO_2. Further to reduce the silica, the magnetically separated taconite is then slurried in water so that the result is about 25% total solids. The taconite slurry is treated with a 1° amine salt of acetic acid by using 0.05 to 0.20 lbs of the amine salt per ton of ore. Air is then bubbled through the slurry.

The silica collects in the froth and is removed from the ore as the froth overflows into the run-off troughs. Table V indicates the effectiveness of coco primary amine acetate as a silica collector in taconite flotation. The results are from a single, rougher flotation test, which accounts for the rather low iron recovery. In actual plant practice, the recovery would typically be 90^+% since most of the iron lost in the tailing can be recovered by a subsequent, cleaner flotation process or by re-circulating the tailings through the grinding and magnetic separation operations.

TABLE V

Magnetically Separated Taconite Before Flotation		Magnetically Separated Taconite After Flotation		
% Fe	% SiO_2	% Fe	% SiO_2	% Fe recovery
64.55	10.16	66.85	7.06	83.2

Some modifications of the amine molecule may produce products which will perform satisfactorily in this application, but it appears that the most satisfactory ones will be primary aliphatic amines with close to 12 carbon atoms.

Solvent Extraction. Solvent extraction is, of course, a broad term. It is used to described a process in which a desirable inorganic, water-soluble species is converted to an organic complex or reaction product that is more soluble in a water-immiscible liquid than in water and hence is capable of being extracted from an aqueous phase. The organic complex which forms may be a typical coordination, noncharged complex or a typical cationic complex.

Solvent extraction is customarily used when the desirable element is present in the ore in low concentration but is extremely valuable.

A process for the extraction of uranium from its ore is used as an example. Typical uranium ores contain 4 lbs of U_3O_8 per ton. In this particular process 1°, 2°, or 3° amines may be used or a typical quaternary ammonium compound. Generally one of the amines will be used, and the 3° amines are favored because of their greater solubility in the organic carrier and oxidation stability. Stepwise the process is as follows.

1. The uranium ore is leached with sulfuric acid by converting the uranium to the water-soluble $UO_2(SO_4)_2^=$ anion. At this point, the acid leach liquor will contain approximately the equivalent of 1.0 g per liter of U_3O_8. The acid leach liquor may also contain as many as 20 other metal ions. By the use of careful techniques such as pH control, control of the oxidation potential of the system, and selection of the amine, it is possible to recover more than 99% of the uranium and at the same time reject nearly all of the other metal ions.

2. The aqueous leach liquor is then extracted with kerosene containing 3 to 6% of tertiary amine and 2 to 5% of isodecyl or tridecyl alcohol, which improves the solubility of the amine in kerosene and aids in the separation of the aqueous and organic layers. The extraction is accomplished by vigorously mixing the aqueous and organic phases and then allowing the two phases to separate. During the mixing operation the $[UO_2(SO_4)_2]^=$ is converted to the cationic salt $[R_3NH]_2[UO_2(SO_4)_2]$, which is soluble in the kerosene layer.

3. After separation of the aqueous and organic phases, the aqueous layer is discarded or sent on for further processing to recover other metals, and the kerosene phase is isolated for stripping. The stripping

of the uranium can be accomplished by extracting the kerosene fraction with 5% aqueous NaCl at a pH of 1. The uranyl amine salt is converted to a water-soluble form of the uranyl sulfate anion, $[UO_2(SO_4)_2]^=$, and the amine hydrohalide is redissolved in the kerosene. At this point, the aqueous layer contains the uranium again but now in a concentration equivalent to 30 to 120 g per liter of U_3O_8 or 30 to 120 times as concentrated as in the original acid leach liquor. The pH of the acid layer is adjusted to approximately 7; NH_3 precipitates a complex uranium salt which is commonly assumed to be $(NH_4)_2U_2O_7$ (4). This salt is collected and processed for the uranium. The kerosene layer with most of the original amine is then recycled and reused; thus the process is quite economical.

Similar types of processes are being used for the recovery of vanadium, molybdenum, and cobalt.

The trilauryl amine and trialkyl (C_{8-10}) amine are ones that have been highly satisfactory for this application to date. It is probable that, as the solvent-extraction technology is developed, it will have an impact on mineral economics similar to that of flotation technology more than 50 years ago.

Uses of Cationic Surfactants

The cationic surface-active agents, in general, are not regarded as good detergents, particularly where cotton detergency is concerned. They do function as emulsifiers, bacteriocides, antistatic agents, and fabric softeners.

Cationics as Emulsifiers. A growing use of cationic emulsifiers is in the preparation of asphalt emulsions. It is essential that a low interfacial tension exist between the asphalt particles and water. Emulsions are made by simultaneously injecting the hot asphalt and the aqueous emulsifier solution into a colloid mill, which shears the asphalt into minute droplets that range from one to five microns in diameter. The emulsifier molecules orient themselves on the surface of these droplets, imparting a positive charge to the surface of the asphalt particles.

Cationic asphalt emulsions are usually composed of from 50 to 70% asphalt and 30 to 50% water with 0.1 to 2% emulsifier. The real objective in emulsifying asphalt is to make a semistable dispersion of asphalt in water. The emulsion should be stable to pumping and prolonged tank storage, but, when contacted with aggregate, either in a mixer or after being deposited on a roadbed, it should break in a matter of minutes.

Cationic asphalt emulsions have the following advantages over anionic systems. They are easier to produce. All that is required is asphalt, water, and emulsifier. Anionics frequently require stabilizing, dispersing, and antistripping agents in addition to the emulsifier. Cationic systems are tolerant of hard water. Cations such as Ca^{++}, Mg^{++}, Fe^{++}, Na^{+}, etc., have essentially no ill effects on emulsion stability. In fact, $CaCl_2$ is sometimes added where extreme long-range stability is required. Anionic systems require soft water or sequestering aids.

Cationics give good stone-coating results over a much wider range of aggregate types. The positive ionic charge on the asphalt droplets insures good coating on all siliceous aggregates whereas anionics are of no value on siliceous types. Cationics will emulsify a wider variety of asphalts. Cationics can be applied in cool weather because cure is not dependent upon the evaporation of water. The strong electrostatic forces between the asphalt droplets and aggregate actually displace the water.

TABLE VI

Compound	Bacteria			
	Gram-Negative		Gram-Positive	
	Escherichia coli	Pseudomonas fluorescens	Bacillus subtilis	Staphlococcus aureus
Phenol	> 1000	> 1000	>1000	>1000
Benzalkonium chloride (standard)	200	300	3	4
(Octyl-decyl) trimethyl ammonium chloride	500	500	50	50
Dodecyl trimethyl ammonium chloride	500	500	5	5
Tetradecyl trimethyl ammonium chloride	150	100	1.5	5
Dodecyl dimethyl benzyl ammonium chloride	750	750	2	2
Coco dimethyl benzyl ammonium chloride	225	225	2	2
Hydrogenated tallow dimethyl benzyl ammonium chloride	2,250	2,250	7	20
Dioctyl dimethyl ammonium chloride	40	775	20	20
Di(octyl-decyl) dimethyl ammonium chloride	50	500	5	5
Didodecyl dimethyl ammonium chloride	2,250	2,250	20	225
Di(hydrogenated tallow) dimethyl ammonium chloride	>2,250	>2,250	225	750
Tri(octyl-decyl) methyl ammonium chloride	500	500	3	5
Tri dodecyl methyl ammonium chloride	>5,000	>5,000	500	1,500

Cationics will coat wet as well as dry aggregates. This prolongs the paving season since small rain showers and morning dew have virtually no effect. Cationics allow quicker opening to traffic because of their unique breaking properties. Cationics have better water-wash resistance immediately after applications. Sudden rain showers are not a serious threat whereas an anionic system may be washed away.

Cationic asphalt emulsions are used in road construction and maintenance primarily as coarse aggregate mixes and seal coatings. Some other applications of cationic emulsions are driveways, parking lots, playgrounds, canal linings, levees, soil stabilizers, and roof coatings. Typical cationic asphalt emulsifiers are the acetates of tallow primary amine, or the tallow diamine derived from tallow primary amine and acrylonitrile.

It is recognized that the above represents only one example of cationic emulsions. The general principles suggest that cationic emulsifiers offer good potential for a wide variety of O/W and W/O emulsion systems.

Cationic Bacteriocides. It is well known that some quaternary ammonium compounds, such as alkyl (C_{12-14}) dimethyl benzyl ammonium chloride and cetyl pryidinium chloride or bromide, possess excellent bacteriostatic or bacteriocidal properties and therefore are useful sanitizers and germicides when properly formulated.

Hueck et al. have recently reported on the screening of 164 fatty nitrogen derivatives for bacteriostatic, fungistatic, and algistatic activity (5). They used alkyldimethyl benzyl ammonium chloride as the standard. Their results indicated that the biostatic activity of the standard is difficult to surpass but that some quaternaries approach it and, in some specific areas, surpass it. Table VI shows a tabulation of some of their data, obtained by a microtechnique roll-culture method (6).

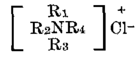
The data in Table VI show that many quaternary ammonium compounds show a significant degree of bacteriostatic activity and that the structure of the molcule has a great deal of bearing upon this activity. Certainly for systems in which emulsification and antimicrobial activity are desired, cationic surfactants offer a wide field of opportunity.

TABLE VII

Compound	Softness rating of fabric with 0.1% of composed based upon weight of fabric[a]
Trimethyl stearyl ammonium chloride	2.8
Di (hydrogenated tallow) dimethyl ammonium chloride	1.2
Tricoco methyl ammonium chloride	2.6
Trilauryl methyl ammonium chloride	3.2
Control	5.0

[a] Softness Rating: 1.0—excellent, 2.0—good, 3.0—fair, 4.0—poor, and 5.0—no softening.

Cationic Fabric Softeners. Quaternary ammonium compounds are used widely as fabric softeners in both the industrial and consumer markets. They are particularly effective on cotton fabric. As indicated earlier, this discussion is confined to the type compounds, and no poly nitrogen-containing compounds are considered. The di long-chain alkyl quaternaries, such as di (hydrogenated tallow) dimethyl ammonium chloride, are preferred as fabric softeners. Table VII shows the results of softening ratings of various softener molecules by the Ashland Chemical test procedure in one test series.



$$\left[\begin{matrix} R_1 \\ R_2NR_4 \\ R_3 \end{matrix}\right]^{+} Cl^{-}$$

The softening test procedure is simply as follows. Eight pounds of desized bath towels are washed in a top-loading, automatic washing machine by using Tide at the manufacturer's recommended concentration. Sufficient fabric softener is added to the final rinse cycle to give 0.1% of active softener, based upon the weight of towels. The towels are dried in an automatic drier and stored for 24 hrs at 77F and 50% relative humidity.

The towels are then rated by a panel of five women three times, and their softness is rated 1 through 5. A rating of 1 is the softest and 5 the harshest; a rating of 5 usually (but not always) is assigned to the untreated control. Four sets of treated towels and one set of untreated towels as control are used in each test. At least one set of the treated towels has always been treated with di (hydrogenated tallow) dimethyl ammonium chloride. The softness ratings are the average of the three ratings given by the five panelists. Each set of towels has therefore been rated 15 times.

The data shown in Table VII clearly indicate the superior performance of the di (hydrogenated tallow) dimethyl ammonium chloride. The alkyl groups should be saturated to reduce the tendency to yellow fabric. Experience has shown that, if the dialkyl chains are C_{12} or higher, good softening results; the C_{16} to C_{18} chain-lengths are preferred. If three long-chain alkyl groups are present in the quaternary molecule, the resulting compound is not easily dispersed in water, and the treated fabric tends to become waterproof.

Hughes and Koch have studied the deposition of di (hydrogenated tallow) dimethyl ammonium chloride on cotton fabric (7). Their results show that the rate and amount of softener deposition is increased by increasing the temperature but that the amount of softener which is deposited tends to level off at 0.1 to 0.2%, based upon the weight of fabric. If concentrations of 0.075% of softener, based upon the weight of fabric, are used, 85 to 95% of the softener which is added will be exhausted onto the fabric. Deposition of the softener tends to be complete within 1 to 3 min. Over a pH range of 3 to 11, softener deposition is satisfactory with a pH of 8.0 as the optimum.

Experience has also shown that, if 0.05 to 0.75% of softener based upon fabric weight is deposited, good softening results are obtained. Concomitantly, when good softening has been attained, the fabric shows a markedly reduced tendency to "cling" to the person in garments made from the fabric, indicating that the presence of the softener has imparted antistatic properties to the material.

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