TABLE 2

Effects of Size of Sample, Amount of Reagent, and Reaction Time with Potassium Iodide in Air on the Peroxide Value of Oxidized Lard

Sample	Weight of Sample, gms.	Solvent, cc.	Saturated KI Solution, cc.	Reaction Time, Min.	Peroxide Value, m. mols
Lard C	0.2	20	0.5	1	7.4
Lard C	0.2	20	1.0	1	8.3
Lard C	0.2	10	0.5	1	7.8
Lard C	0.2	10	0.5	2	8.1
Lard C	0.5	20	1.0	2	8.2
Lard C	5.0*	50	1.0	1	6.5
Lard C	5.0**	30	0.5	2	6.2
Lard D	0.5	20	1.0	2	28.2
Lard D	1.0	20	1.0	2	26.4
Lard E	0.5	20	1.0	2	22.9
Lard E	1.0	20	1.0	2	21.2
Lard E	2.0	20	1.0	2	19.9
Lard F	0.5	20	1.0	2	29.6
Lard F	5.0**	30	0.5	2	26.2
Lard G	0.2	20	1.0	1	38.3
Lard G	5.0**	30	0.5	2	32.4
Lard H	0.5	20	1.0	2	70.1
Lard H	5.0**	30	0.5	2	63.7
Lard I	0.2	20	1.0	1	4.1
Lard I	0.5	20	1.0	2	4.0
Lard I	5.0*	50	1.0	1	3.3
Lard I	5.0**	30	0.5	2	3.3

* Wheeler's method (3).
** Wheeler's method as used by King, Roschen, and Irwin (1).

peroxide values, as shown in Table 2. These differences are shown to be of minor significance, however, when the peroxide values are plotted against time to estimate the stability, especially when the tests were carried out at elevated temperature and with aeration.

Summary

An all-glass aeration tube and improved air-distributing apparatus are described for use in the Swift stability test or similar accelerated method of determining stability of fats.

A procedure is described in which only one tube is required for each test sample. By this procedure, it is possible to carry out as many stability tests simultaneously on one standard apparatus as on three such units by the usual three-tube method.

Observations on the use of adaptations of Wheeler's method of determining peroxide values are reported. The effects of air, time of reaction, size of sample, and quantities of reagents were investigated.

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The Detergent Properties of Bactericidal Fatty Acid Derivatives

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New types of quaternary ammonium derivatives have been recently introduced by Epstein and Harris (1) as bactericidal agents. From a chemical and physico-chemical standpoint, these new compounds may be characterized in the following manner: First, one relatively high molecular weight organic radical and three relatively low molecular weight organic radicals are attached to pentavalent nitrogen. Second, the organic portion of the molecule is the cation, i.e., charged positively; the inorganic portion attached to the pentavalent nitrogen is the anion, i.e., charged negatively. Third, the total mass of the lipophile groups in the cation are of such magnitude and so orientated in relation to the hydrophile groups, as to produce the proper lipophile and hydrophile balance* of the groups in the molecule, which according to Harris (2), endows the compound with interface modifying properties. Fourth, the high molecular weight radical, which is attached to the pentavalent nitrogen contain carboxyl $\left[\begin{matrix}O\\ \|\\ -C-OH\end{matrix}\right]$ and amide $\left[\begin{matrix}O\\ \|\\ -C-NH-\end{matrix}\right]$ linkages. The structures of these new types of compounds are shown in Table I.

The fatty acid esters of the pyridinium derivatives (compound No. 5, Table I), designated as E 607, were selected for our present investigation. A study was made to determine first, the effect of varying the number of carbon atoms in the fatty acid radical on the bactericidal value and detergency of the homologous compounds. Second, a study was made of the comparative detergent potency of the quaternary ammonium derivative containing carboxyl and amide groups in the molecule, and of quaternary ammonium compounds which do not contain carboxyl and amide linkages. Third, the detergent potency of the quaternary ammonium compounds was compared with that of soap and certain other alkaline detergents.

The homologous series of the E 607 compounds, N—(acyl esters of colamino formyl methyl) pyridinium chloride, was prepared from fatty acids of C_8, C_{10}, C_{12}, C_{14}, C_{16} and C_{18}, according to methods described by Katzman (3). The phenol coefficient of each of the homologous compounds was determined at 20°C. and 37°C. respectively, according to the official F.D.A. method (4), using Staphylococcus aureus and Eberthella typhosa as test organisms. The results are tabulated in Table II.

* The nature of "balance" in interfacially active molecules and a method for measuring "balance" are described in the cited Harris patents. A further discussion of "balance" is to be found in the book and journal literature, particularly:

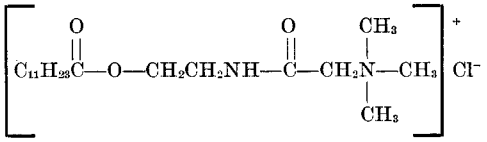
Clayton—"Theory of Emulsions," pg. 101—P. Blakiston's Son & Co., Philadelphia, Pa. (1935).

Hefter-Schonfeld—"Chemie und Technologie der Fette und Fettprodukte," vol. 2, pp. 755, 756—Verlag von Julius Springer, Vienna, (1937).

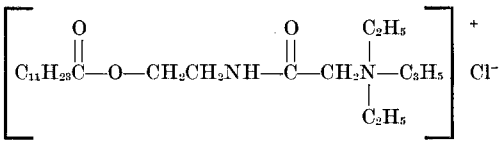
Snell—"Surface Active Agents"—Industrial and Engineering Chemistry, Vol. 35, No. 1, pp. 107-117 (1943)—this is a comprehensive review of the field and contains more than a dozen references to "balance."

TABLE I

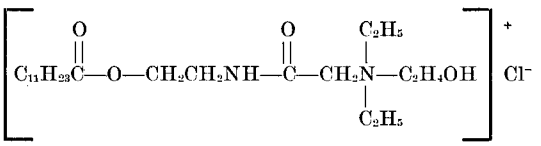
N—(higher acyl esters of colamino-formyl methyl) quaternary ammonium halides

(1) 

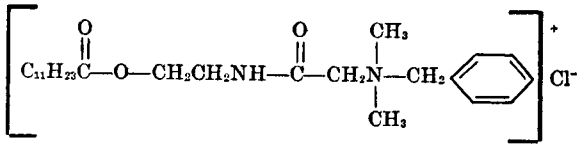
N—(Lauric acid ester of colamino-formyl methyl) trimethyl ammonium chloride.

(2) 

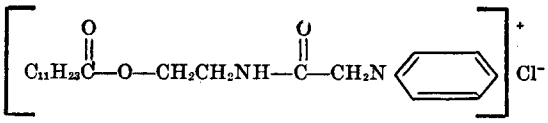
N—(Lauric acid ester of colamino-formyl methyl) triethyl ammonium chloride.

(3) 

N—(Lauric acid ester of colamino-formyl methyl) diethyl hydroxyethyl ammonium chloride.

(4) 

N—(Lauric acid ester of colamino-formyl methyl) dimethyl benzyl ammonium chloride.

(5) 

N—(Lauric acid ester of colamino-formyl methyl) pyridinium chloride.

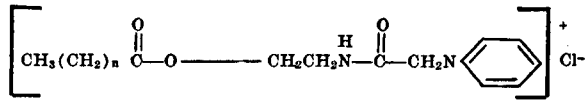
The purity of the substances listed in Table II may be judged by the following data:

	Per cent Ionic Chlorine Theory	Per cent Ionic Chlorine Found
C_8	10.35	10.30
C_{10}	9.57	9.54
C_{12}	8.89	8.70
C_{14}	8.25	8.18
C_{16}	7.80	7.72
C_{18}	7.47	7.43

In the homologous series of the pyridinium chloride derivatives with which this report deals, it has been found that in varying the length of the carbon chain of the fatty acids from C_8 to C_{18}, the maximum bactericidal activity was obtained when the compound contained the fatty acid radical of C_{14}. The phenol coefficient of this compound for S. aureus at 20°C. is 500, and at 37°C., it is 785. The lowest bactericidal value was obtained with the compound containing the C_8 fatty acid radical. The phenol coefficient of this latter compound for S. aureus at 20°C. is 6, and at 37°C., it is 11. The same relations held good for the C_{14} and C_8 compounds when E. typhosa was used as test organism at 20°C. and 37°C., respectively. For the two test organisms used, one of which is a gram positive and the other a gram negative, at the two temperatures used, the sequence of increasing phenol coefficients in the homologous series of compounds tested, is practically the same; namely, C_8, C_{10}, C_{18}, C_{16}, C_{12}, and C_{14}. The only exception noticed is in the case of E. typhosa, at 20°C.; compound C_{10} follows the C_{18} compound. However, the difference in the phenol coefficients is only slight; namely, the C_{10} compound has a phenol coefficient of 22, and the C_{18} has a phenol coefficient of 16. It is also noted that the phenol coefficients of all compounds tested at both temperatures are higher for S. aureus (a gram positive organism) than for E. typhosa (a gram negative organism). A commercial pyridinium ammonium derivative designated as E 607 Special, was prepared according to Katzman's (3) method using a mixture of C_{12} and C_{14} fatty acids. The phenol coefficient of

TABLE II

The Effect of Varying the Length of the Carbon Chain in the Acyl Radical on the Phenol Coefficients
The Effect on Killing Power by Changing the Carbon Chain in the Fatty Acid Radical of E 607 Compounds



Number of carbons in $CH_3(CH_2)_nC(=O)-O-$	Average maximum dilution which kills organism in 10 minutes				Phenol coefficients			
	20°C.		37°C.		20°C.		37°C.	
	S. Aureus	E. Typhosa	S. Aureus	E. Typhosa	S. Aureus	E. Typhosa	S. Aureus	E. Typhosa
8	1: 350	1: 550	1: 800	1: 1,300	6	6	11	8
10	1: 2,750	1: 2,000	1: 3,500	1: 4,000	45	22	19	25
12	1: 14,000	1: 10,000	1: 25,000	1: 30,000	232	111	355	187
14	1: 30,000	1: 30,000	1: 55,000	1: 55,000	500	333	785	343
16	1: 7,000	1: 3,500	1: 9,000	1: 11,000	116	38	116	68
18	1: 4,000	1: 1,500	1: 7,000	1: 6,000	66	16	100	38
Mixture of C_{12} and C_{14}	1: 30,000	1: 20,000	1: 40,000	1: 5,500	500	222	571	343

*According to F.D.A. Official Method.

this product was tested and the data obtained tabulated at the bottom of Table II.

The results of the test indicate that the phenol coefficient of the mixture of the C_{12} and C_{14} compounds when tested against S. aureus at 20°C. is 500, exactly the same as for the C_{14} compound. The addition of C_{14} compound to the C_{12} compound, which has lower bactericidal potency, brings the latter up to the bactericidal level of the C_{14} compound. The same phenomenon takes place at 37°C. when the test is made against E. typhosa. The phenol coefficient of the C_{12} compound is 187; of the C_{14} compound, 343; and of the mixture of C_{12} and C_{14} compounds, also 343. Thus, the addition of C_{14} compound to the C_{12} enhances the bactericidal potency of the latter to the higher level of the C_{14} compound. In the case of E. typhosa, when tested at 20°C., and S. aureus when tested at 37°C., the addition of C_{14} compound to the C_{12} raises the phenol coefficient of the C_{12}, but does not reach the higher bactericidal level of the C_{14} compound.

Several of the compounds tabulated in Table II were selected for a study of their respective detergent properties. The test consists of washing standard soiled cloths in a Launder-Ometer, and in determining the degree of brightness or reflectance of the surface of the washed soiled cloths by means of a Photovolt Reflectometer. The details of the procedure used in these experiments are as follows:

Wool flannel strips were soiled using a soil "solution" consisting of a suspension of .0625 grams A.O.C.S. tallow and 3 grams A.O.C.S. cylinder oil, in 1500 c.c. of carbon tetrachloride. Soiling was accomplished by immersing the fabric in the soiling "solution" by hand thirty times. The soiled cloths were dried in an oven to evaporate the solvent.

In order to obviate, as much as possible, variations in the amount of soil on the test cloths (5), several yards of cloth were soiled, cut into small swatches, and all washing tests were made on the same soiled cloth. The results obtained are of an arbitrary character but comparable among themselves.

Squares of cloth, four inches on a side, were used for the tests. The test pieces were placed in glass jars containing ten ⅜-inch rubber balls and 200 c.c. of the test solution. The water used for all these tests was of zero hardness. The jars were clamped into the rotating arms of the Launder-Ometer, and rotated at a constant speed of 42 revolutions per minute, at 25° Centigrade for five minutes.

After treating with the detergent solution, the samples were rinsed in water, and dried in a hot air oven. The degree of brightness of the washed cloths was determined by a Photovolt Reflectometer using a green filter. The instrument is set so that the soiled cloth washed in tap water represents a brightness or reflectance of 0% and the clean unsoiled cloth washed in tap water under the same conditions, represents a brightness or reflectance of 100%. Readings are then taken on the other soiled test cloths washed in the various detergent solutions. These readings fall on the instrument between 0% to 100%, depending upon the effectiveness of the detergent solution in which the soiled cloth was washed. The readings on the instrument represent relative percentages of light reflectance or brightness on the surface of a given soiled cloth washed in a detergent solution, in relation to the reflectance or brightness of light on the surface of the same type of cloth similarly soiled and washed in water, and the brightness of the clean unsoiled cloth washed in water. The readings on the instrument express the relative amount of dirt removed, and hence give a relative idea of the detergent value of the solution in which the soiled cloths are washed. The higher the reading, the greater the detergent value of the test solution. Four readings were made on each sample of cloth, using four thicknesses of the fabric for the reading of the surface reflectance.

The results of the washing test are tabulated in Table IV. The soiled cloths were washed in .03% solution of the quaternary ammonium derivatives. The test shows that there is practically no difference in the detergent properties of the compound E 607 M and E 607 Special. Under the conditions of the ex-

TABLE III

A Graphic Representation of Data of Table II Showing the Relation of the Number of Carbons in the Fatty Acid Radical to the Bactericidal Potency of the Homologous Compounds

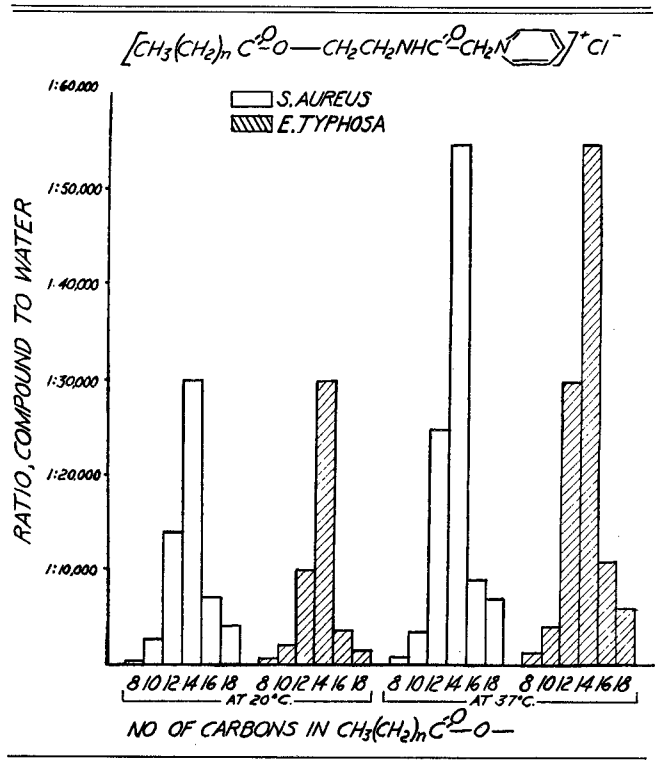


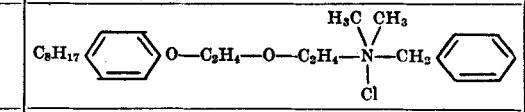
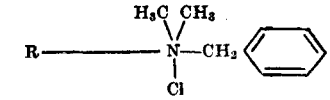
TABLE 4

Relative Detergency Values Expressed in Percentages of Reflectance of Wool Cloth as Compared With Washed Soiled and Washed Unsoiled Cloth. Washing Test Five Minutes. Results Are Average of Four Readings for Each Cloth on Photovolt Reflectometer.

Substance used	Per cent of reflectance	
	Washing at 25°C.	Washing at 37°C.
.03% E 607 M C_{14} Fatty acid ester of colamino formyl methyl pyridinium chloride	31	34
.03% E 607 Spl. Mixture of C_{12} + C_{14} fatty acid ester of colamino formyl methyl pyridinium chloride	34	37
.03% Alkyl dimethyl benzyl ammonium chloride	16	16
.03% Alkyl dimethyl benzyl ammonium chloride plus 1% tri sodium phosphate	14	19
.1% Soap (Low Titre)	8	9
.2% Soap (Low Titre)	12	11

TABLE 5

Detergency Test Made Under Similar Conditions as in Table 1
(Washing five minutes)

Substance	Carbon chain length of fatty acid radical	Per cent concentration	Per cent reflectance washing at 37°C.
E 607	C_{12}	.06	51
E 607 M	C_{14}	.06	47
E 607 Spl	$C_{12} + C_{14}$	.06	45
E 607 Stearic	C_{18}	.06	36
E 607—O	Oleic	.06	54
E 607 Spl + E 607 St.	$C_{12} + C_{14} + C_{18}$	.06	61
p-tertiary-octyl-phenoxy-ethoxy-dimethyl-benzyl-ammonium-chloride		.06	25
Alkyl-dimethyl-benzyl-ammonium-chloride		.06	22
Tap water (zero hardness) soiled cloth			0
Tap water (zero hardness) unsoiled cloth			100

periment, there seems to be no difference in detergency in the compound prepared from C_{12} and C_{14}, although as seen from Table II, there is a decided difference in the bactericidal potency of these two compounds.

The compounds E 607 M and E 607 Special, in .03% solution, possess twice as much detergent value as the "alkyl dimethyl benzyl ammonium chloride" when used in similar concentrations. Even when 1% of trisodium phosphate was added to the latter, the reflectance was 14, as against 34 for E 607 Special. The raising of the washing temperature from 20°C. to 37°C. did not have any appreciable effect upon the detergency. The detergent power of .03% solution of the 607 M and 607 Special compounds is about four times as great as that of .1% soap solution, used under the same test conditions, and three times as great as compared with .2% soap. These experiments indicate the superiority of the detergent value of the C_{12} and C_{14} fatty acid esters of colamino formyl methyl pyridinium chloride, when compared with soap or another quaternary ammonium derivative, namely, "alkyl dimethyl benzyl ammonium chloride."

In Table V are tabulated the results of the washing test when .06% detergent was used. These tests show that there is practically no difference in the detergent value of the compound of the E 607 series prepared from C_{12}, C_{14}, or a mixture of C_{12} and C_{14} fatty acids. The compound, E 607 Stearic, prepared from C_{18} fatty acids possesses approximately ⅔ of the detergent values of the C_{12} and C_{14} members of the homologous series. However, a mixture of C_{12}, C_{14} and C_{18} derivatives of the E 607 series possesses the highest detergent value, and gives a reflectance reading of 61 as against 47 for the C_{14} compound.

A comparison of the detergent properties of the E 607 series prepared from C_{12}, C_{14} and C_{18} (oleic) fatty acids respectively, and mixtures of C_{12}, C_{14} and C_{18} fatty acids show that when used in .06% concentration, they possess about twice the detergent properties of other quaternary ammonium derivatives, such as "alkyl dimethyl-benzyl ammonium chloride," and tertiary-octyl-phenoxy-ethoxy-dimethyl-benzyl-ammonium chloride. The same results were obtained when .03% solutions were used in the comparative tests. It appears that the presence of a carboxyl and amide linkage in the compound of the E 607 series has a decided effect in imparting greater detergent potency. These compounds are also very good foamers, even in very dilute solutions. They are colorless, odorless, non-irritating to the skin and possess a very low "toxicity index" (6), (7).

Summary

1. A study was made of the bactericidal values of a homologous series of fatty acid esters of colamino formyl methyl pyridinium chlorides, varying the fatty acids from C_8 to C_{18}.

2. The compounds prepared from C_{14} fatty acid possess the highest phenol coefficients; 500 for S. aureus, and 333 for E. typhosa, 20°C.; and at 37°C., 785 for S. aureus and 343 for E. typhosa. The compounds prepared from C_8 fatty acid possess the lowest phenol coefficients.

3. Detergent tests were made on some of the members of the homologous series. The results show that the compounds prepared from C_{12}, C_{14} and C_{18} (oleic) fatty acids and mixtures thereof, are considerably superior in detergency to soap and about twice as effective when compared with other quaternary ammonium compounds which do not have carboxyl and amide linkages in the molecule.

4. There seems to be no correlation between detergency and bactericidal function.

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