

fats in which it is effective. The converse proposition also holds; if an acid like ascorbic, citric or phosphoric is effective in a natural fat one may be fairly certain that the fat also has a naturally occurring phenolic inhibitor in it. Much work remains to be done to identify the characteristics of some of the more obscure antioxidants, like those released from seed cakes by acetic acid (29), those found in various flours (30), the polymerization products in heated sugars, perhaps di-enols (31), or those found in rice bran extracts (32).

WE MUST admit that empirical facts are more abundant than logical explanations, but the facts must be obtained with care and must be closely scrutinized. Needless to say the manner of preparation of the fat substrates and the relative purity of the various components of the system may greatly modify the results obtained. For example, the successful stabilization of lard by soy bean phospholipids (26) is not valid evidence against the thesis here proposed; the soy bean phospholipids contained traces of admixed tocopherols and the combined effectiveness was increased by addition of more tocopherol, of ascorbyl esters, or of both.

Even though we know only in part, it is possible to set up a few fundamental principles in stabilization. If the fat in question naturally has an optimum content of some phenolic antioxidant, the addition of further amounts may be useless; it may even be detrimental as in the case of tocopherols because they are also vulnerable to oxidation; the quality of the fat may be depreciated by the oxidation products of phenolic inhibitors. Such fats can be benefited by the addition of synergists which prolong the action of the phenolic stabilizer and make a little of it go farther.

By the same token, the addition of a phenolic inhibitor to an animal fat should not be overdone. It

is wise to add as little as necessary and to reinforce what is added by the simultaneous addition of synergists alone or in combination. Intensive study of the action of synergists on the phenolic inhibitors and upon each other promises to be highly interesting in theory and fruitful in practice.

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Detergency Studies at Low Solution Concentrations¹

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PREVIOUS studies of the detergency efficiencies of soap and alkaline soap builders (1, 2) have been made in both soft and hard water, but at solution concentrations varying from 0.10-0.20% in 50 p.p.m. soft water and from 0.27-0.32% in 300 p.p.m. hard water. Other studies with synthetic detergents and builders have been made in water of varying hardness and in sea water, but generally at rather high levels of solution concentration (3, 4). Several investigators have made tests of soap at 0.1% concentration to which varying concentrations of alkaline builders have been added, one using an especially constructed small laboratory washer (5) and another (6) utilizing both a Launderometer and a small (24 x 40 inch) monel wash wheel.

General power laundry practice is to reduce the concentration of the soap and alkali combination as the clothes become cleaner, i.e., to use the largest amounts of detergent at the periods when the greatest amounts of soil are present, thus varying the concentration throughout the wash formula. Consequently, soap solution concentrations may vary (7) from approximately 0.15% to 0.01%, and the builder concentrations from 0.09% to 0.012%. Detergency results under such conditions have been fairly well established, but similar work with synthetic detergents has not been undertaken. Other than the data published for Santomerse combined with certain alkaline builders (4) the little information which has been given regarding the detergency efficiency of synthetic agents combined with alkalies deals with relatively high solution concentrations. Tests were therefore un-

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dertaken to determine the effect produced by such combinations in hard and sea water at levels of low solution concentrations.

The technic used in obtaining the present detergency results has been thoroughly described (2). Any variations therefrom will be noted in the section in which such variation was made. The standard soil used comprised Oildag, Wesson oil and carbon tetrachloride applied in standard manner to desized white Indianhead fabric. All individual tests were made in duplicate in the Launderometer. Included in each of the three to six series of duplicate tests was a comparison detergent.

Materials Used

Santomerse No. 1—contains 40% active ingredient comprised essentially of dodecylbenzene sodium sulfonate

Santomerse No. 3—comprising 99% + dodecylbenzene sodium sulfonate

Tetrasodium Pyrophosphate (TSPP)—anhydrous, commercial

Trisodium Phosphate (TSP)—hydrated, commercial

Sodium Carbonate—C. P. anhydrous grade

Sodium Orthosilicate—anhydrous, commercial grade

Sodium Metasilicate—pentahydrate, commercial grade.

A synthetic sea water (8) of the following composition was used for the sea water tests:

Magnesium chloride (MgCl ₂ ·6 H ₂ O).....	12.0 g./Liter
Calcium chloride (CaCl ₂).....	2.5 g./Liter
Sodium sulfate (Na ₂ SO ₄).....	4.0 g./Liter
Sodium chloride (NaCl).....	25.0 g./Liter

This composition was made up to 500 ml. for double concentration. The samples were dissolved in distilled water and sufficient of the double concentrated sea water was added to yield the desired solution concentration in single strength sea water.

Sea Water Tests

In these tests a solution concentration of 0.05% at 140°F. was arbitrarily chosen, and only combinations of tetrasodium pyrophosphate with either Santomerse No. 1 or Santomerse No. 3 were tested.

The results of these tests are shown in Figure 1. This figure shows graphically that TSPP alone removes more soil at this solution concentration than either Santomerse No. 1 or No. 3, but that an optimum removal is obtained with a composition comprising approximately 80% TSPP and 20% Santomerse. It is of decided interest that TSPP should possess such relatively high detergency when not combined with a surface active agent. The effect of dilution of active ingredient is shown by comparison of the combinations containing Santomerse No. 1 with those containing Santomerse No. 3. The detergency of the combinations containing Santomerse No. 3 tend to be slightly superior to those containing Santomerse No. 1 where least TSPP is used, otherwise differences are negligible.

It is noteworthy that even though the pH values for the TSPP-Santomerse combinations lie in the range of 6.2 to 6.5, and that there is negligible lather, detergency is maintained at a high level when 60% or more of TSPP is used. The use of a low solution concentration in sea water is advantageous in that thereby the amount of insoluble salt formed is minimized; hence there is less tendency for insoluble salts to remain in the article being cleansed.

Hard Water Tests

PREVIOUS tests (4) have shown that extremely hard water will consume Santomerse by forming the insoluble calcium salt as evidenced by detergency

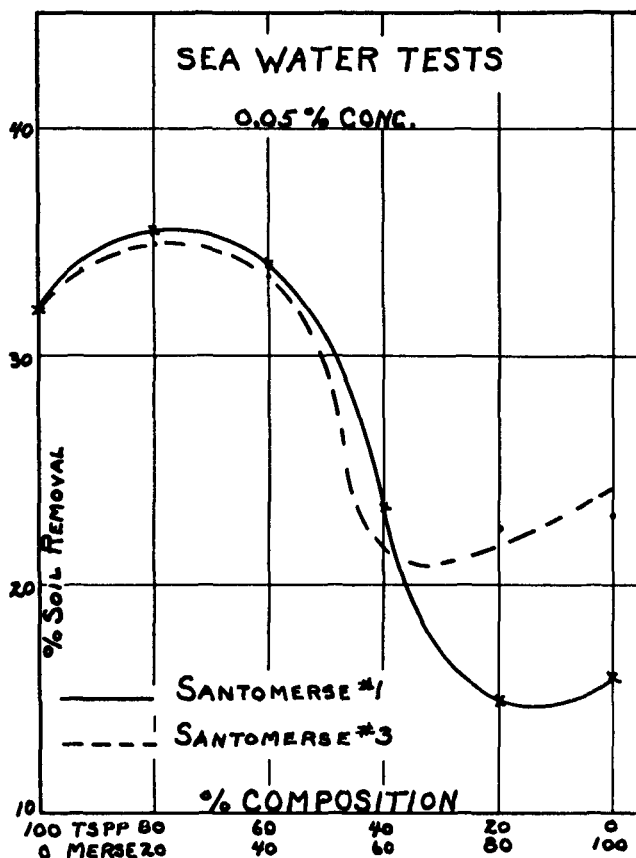


Fig. 1. Sea water tests. 0.05% concentration.

Sample	% Compo.	Santomerse No. 1		Santomerse No. 3	
		pH	Suds (Ins.)	pH	Suds (Ins.)
TSPP.....	100	6.2	0	6.4	0
TSPP.....	80	6.2	tr.	6.5	tr.
Santomerse.....	20				
TSPP.....	60	6.2	tr.	6.4	½
Santomerse.....	40				
TSPP.....	40	6.2	tr.	6.5	tr.
Santomerse.....	60				
TSPP.....	20	6.2	tr.	6.4	tr.
Santomerse.....	80				
Santomerse.....	100	6.2	0	6.3	tr.

data, but that relatively small excesses of the detergent can be used to overcome this hard water effect. Data was also shown indicating that TSPP and TSP would improve detergency markedly. These tests were made, however, at solution concentrations of from 0.18% to 0.60%. No attempt had been made to test such combinations at lower concentrations in a single, relatively high water hardness.

The present tests were made under the conditions already described and with a synthetic hard water whose hardness was composed of 60% calcium and 40% magnesium (as calcium chloride and magnesium sulfate). A solution concentration of 0.075% was chosen because this represented a point about midway between the extremes used for soap and builder combinations and at the same time was thought to be sufficient to produce an acceptable degree of soil removal.

The first series of tests was made on the anhydrous basis because dry compositions were contemplated. Sodium sulfate was used as a diluent since it is a concomitant of detergent manufacture and has only minor effect upon detergency. The percentage of ac-

tive ingredient was maintained constant at 40% of the composition throughout these tests.

The "Average Soil Removal" is a weighted basis for comparison, while "Cumulative Soil Removal" represents the actual whiteness of the swatch after four ten-minute washes. The cumulative value therefore more nearly represents the final effect obtained by a multiple-suds operation and in no case does this value change the relative order of effectiveness of the materials tested.

The results of these wash tests are shown in Table I. The combinations may be arranged in the following order of decreasing efficiency (listing only the alkaline builder):

TSP
 TSPP
 TSPP—Orthosilicate (1:1)
 TSPP—TSP (1:1)
 Orthosilicate and metasilicate
 Sodium carbonate

All of these compositions are improvements over the equivalent amount of Santomerse No. 1.

TABLE I
 Wash Test Data
 0.075% Concentration (dry basis)
 300 p.p.m. Hard Water

No.	Materials	Compo.	Average % Soil Removal	pH	Suds (Ins.)	Cumulative % Soil Removal
1	Santomerse No. 3.... Na ₂ SO ₄ TSP.....	40 20 40	39.0	9.2	¼	47.0
2	Santomerse No. 3.... Na ₂ SO ₄ TSPP.....	40 20 40	35.0	7.1	3	42.0
3	Santomerse No. 3.... Na ₂ SO ₄ TSPP..... Orthosilicate.....	40 20 20 20	34.0	10.2	3	41.0
4	Santomerse No. 3.... Na ₂ SO ₄ TSPP..... TSP.....	40 20 20 20	30.5	8.9	3	39.0
5	Santomerse No. 3.... Na ₂ SO ₄ Orthosilicate.....	40 35 25	29.2	9.6	¼	34.0
6	Santomerse No. 3.... Na ₂ SO ₄ Orthosilicate.....	40 20 40	27.5	10.5	¼	34.0
7	Santomerse No. 3.... Na ₂ SO ₄ Metasilicate.....	40 20 40	29.0	9.9	¼	33.0
8	Santomerse No. 3.... Na ₂ SO ₄ Sodium carbonate...	40 20 40	15.5	9.7	tr.	18.0
9	Santomerse No. 1....	100	12.5	6.7	¼	16.5

A further series of test was made, this time on the "as received" basis, but the ratios of Santomerse No. 1 to the alkaline builders were maintained at 67:33 and 75:25, and besides tests at 0.075% concentration additional tests were made at 0.10%. These tests would represent mechanical mixtures of Santomerse No. 1 and alkali of 2:1 and 3:1 ratios, such as might be added directly to a wash wheel. In these cases it is obvious that the ratio of synthetic active ingredient was varied from the 40% basis of the data given in Table I. The results of these tests are shown in Tables II and III. Arrangement of the alkalies in decreasing order of effectiveness was the same as for Table II:

TSP
 TSPP
 Metasilicate
 Sodium carbonate

TABLE II
 Detergency
 300 p.p.m. Hard Water
 Materials "as received" Basis
 0.075% Concentration

No.	Materials	Compo.	% Soil Removal	pH	Suds (Ins.)	Cumulative % Soil Removal
1	Santomerse No. 1....	100	12.5	5.8	¼	16.5
2	Santomerse No. 1.... TSPP.....	67 33	26.0	6.8	1	32.0
3	Santomerse No. 1.... TSPP.....	75 25	28.0	6.7	1	33.0
4	Santomerse No. 1.... Metasilicate.....	67 33	22.0	9.5	¼	27.0
5	Santomerse No. 1.... Metasilicate.....	75 25	17.0	9.6	tr.	21.0
6	Santomerse No. 1.... Soda Ash.....	67 33	13.5	9.6	¼	14.5
7	Santomerse No. 1.... Soda Ash.....	75 25	16.0	9.7	tr.	19.0
8	Santomerse No. 1.... TSP.....	67 33	29.5	8.1	tr.	34.0
9	Santomerse No. 1.... TSP.....	75 25	28.0	8.0	¼	34.0

With the exception of the metasilicate compositions, in which increased amounts of the silicate resulted in improved detergency, there are no marked differences between the 75:25 and 67:33 mixtures in which the same alkali is used, nor are there appreciable differences between tests made at 0.075% and 0.10% solution concentration.

Detergency Testing of Builders

THE previous tests showed that Santomerse No. 1 without added alkali is a relatively poor detergent at these low solution concentrations. Since the addition of alkalies seemed to improve detergency so markedly, tests were made to determine the effect produced by the alkalies alone. Such tests had not previously been made because there had been no indication that these alkalies possessed a high degree of detergency. As a matter of fact, the percentage soil removal for the combinations is not high, and is only high in comparison with Santomerse No. 1 at 0.075%.

TABLE III
 Wash Test Data
 0.10% Concentration
 300 p.p.m. Hard Water
 Materials—"as received" basis

No.	Materials	% Compo.	% Soil Removal	pH	Suds (Ins.)	Cumulative % Soil Removal
1	Santomerse No. 1....	100	15.0	5.5	¼	20.0
2	Santomerse No. 1.... TSPP.....	67 33	27.5	6.9	3	34.5
3	Santomerse No. 1.... TSPP.....	75 25	27.0	6.8	3	35.5
4	Santomerse No. 1.... Metasilicate.....	67 33	21.0	9.6	½	27.5
5	Santomerse No. 1.... Metasilicate.....	75 25	17.5	9.7	¼	24.5
6	Santomerse No. 1.... Soda Ash.....	67 33	15.0	9.7	¼	19.0
7	Santomerse No. 1.... Soda Ash.....	75 25	14.0	9.8	¼	20.5
8	Santomerse No. 1.... TSP.....	67 33	31.0	8.2	¼	35.5
9	Santomerse No. 1.... TSP.....	75 25	29.0	8.4	½	36.5

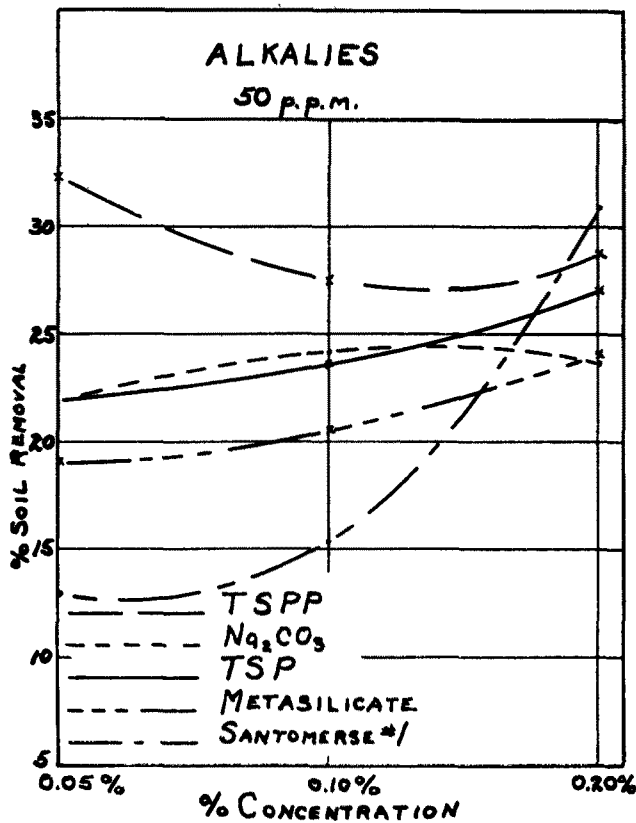


FIG. 2. Alkalies alone. 50 p.p.m. water.

It should be pointed out that water alone results in approximately the same degree of soil removal (7-12%).

The tests with the alkalies were made on the "as received" basis since they had been so used in the previous tests in combination with Santomerse, and in this form are most generally used by industry. Concentrations of 0.05, 0.10 and 0.20% in 50 p.p.m. and 300 p.p.m. synthetic water hardness were chosen, and the test results are shown graphically in Figures 2 and 3.

Soft Water. TSP, metasilicate and sodium carbonate fall into an intermediate group within the same general range throughout, with metasilicate in the lower range at 0.05 and 0.10% concentrations. TSP tends to remove more soil than the other materials and shows the unusual characteristics of removing more soil at 0.05% than at the higher concentrations.

Hard Water. There are no essential differences in any of the alkalies in hard water, and in general detergency is reduced as the concentration is lowered.

Peptization Values

It may be suggested that the type of soil involved would be more readily susceptible to removal by an alkali than by a neutral product because of the presence of saponifiable matter, but the fact is that certain neutral products in extreme dilution are also effective soil removers, the extent of removal depending considerably upon the sensitivity of the detergent to dilution. A possible reason for the efficiency of the alkalies is their ability to peptize carbon particles and oil globules. It is recognized that TSP and metasilicate are excellent cleansers for oil covered surfaces, so that they also should tend to peptize the mineral oil present in this standard soil even though they are

poor surface tension reducers. Since the washing process consists of reduction in the affinity of the soil for the surface to be cleansed, with suspension of sufficient duration that the soil may be rinsed or flushed away, agents which exert superior peptizing action should show up well in this test. An attempt was therefore made to correlate soil removal and peptization.

A test used for evaluating the peptizing action of alkalies follows:

Method. 99 ml. of water to which had been added the required amount of dispersing agent was transferred to a 4 oz. oil sample bottle. To the solution was added 1.00 g. of burnt umber (pigment grade). The bottles were then shaken 25 times, placed in a rack, and aged in a cabinet free from vibration. At the end of 20 hours the tip of a 25 ml. pipette was placed in the geometrical center of the bottle and 25 ml. of suspension withdrawn. The iron content was determined by the dichromate method and the amount of suspended umber in the sample was calculated. This value was multiplied by four to give the milligrams of umber per 100 ml. of solution. All tests were conducted at room temperature and were made in triplicate. The average of the three results are reported.

The data for this test obtained with TSP, TSPP, sodium carbonate, metasilicate and Santomerse No. 1 are shown in Figure 4. The results of these tests show that TSPP and metasilicate have a high degree of dispersing ability over the concentration range. TSP lies in the same general range at the two lower solution percentages, but is lowered markedly at 0.2%, probably as a concentration effect. Both Santomerse No. 1 and sodium carbonate are of an extremely low order of efficiency. As a result of this evaluation the materials may be arranged in the following general order of decreasing effectiveness:

TSPP	Santomerse
Metasilicate	Sodium carbonate
TSP	

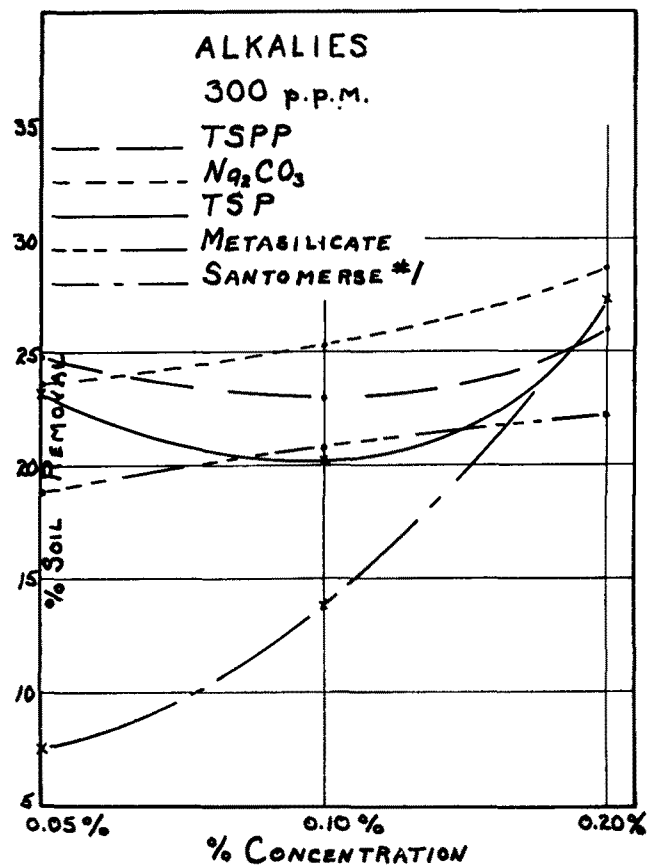


FIG. 3. Alkalies alone. 300 p.p.m. water.

This order is slightly at variance with those obtained in the detergency tests of the alkalies in combination with Santomerse No. 1. It is in fair agreement with the detergency results for the builders alone in soft water, but the correlation is poor for hard water where the detergency results exhibited no evidence of marked variation between the alkalies. It is hardly to be expected, however, that there should be exact correlation between two such dissimilar systems as graphite-mineral oil-vegetable oil and degreased burnt umber. The fact that certain of the builders exhibited high effectiveness in each of several series of tests is an indication that these materials would probably be effective for removal of soils under a variety of use conditions.

Summary

Tests made with mixtures of Santomerse No. 1 or No. 3 with TSPP at 0.05% (in synthetic sea water) indicate optimum soil removal for combinations of 80% TSPP and 20% Santomerse. At this solution concentration TSPP alone removed more soil than either Santomerse product.

Tests made in hard water at 0.075% solution concentration with Santomerse combined with various alkaline soap builders in 1:1 ratios of Santomerse No. 3 to anhydrous alkaline builders permitted arrangement of the alkalies in decreasing order of effectiveness as follows:

- TSP
- TSPP
- TSPP—Orthosilicate (1:1)
- TSPP—TSP (1:1)
- Orthosilicate and metasilicate
- Sodium carbonate

Further tests at the same solution concentration were made with hydrous builders on an "as received" basis but with Santomerse No. 1 to builder ratios of 67:33 or 75:25. The order of efficiency of the builders was the same as for the previous tests, and there were negligible differences between the two ratios tested.

Detergent testing of several of the alkaline soap builders indicated relatively high soil removal at low solution concentrations in comparison with Santomerse No. 1 and accounts for improved detergency of its mixtures with alkali.

Burnt umber peptization values tend to corroborate detergent findings.

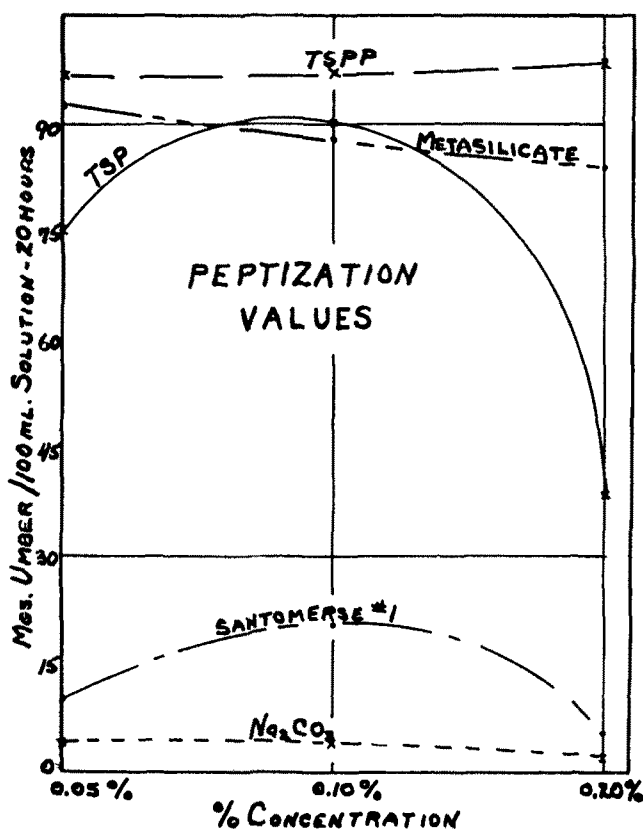


FIG. 4. Peptization values. Milligrams of Suspended UMBER/100 ml. solution.

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The Gravimetric Determination of Foreign Material in Cellulose Fibers

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Summary

A METHOD is offered for the gravimetric determination of foreign material in cellulose fibers which is particularly applicable to cottonseed linters, fiber, and notes. The procedure is relatively simple and rapid, requiring only equipment and technique generally in use in the cottonseed industry's laboratories. Determinations are reproducible within significant limits. The foreign material, seed, hulls, hull bran, etc., is recovered (excepting particles finer

than 50 mesh) so that it can be examined and its nature classified as to type. Use of the method would give the lint producer a dependable index to relative lint cleanliness, and the effect of modifications in seed cleaning and lint room operation aimed at improved lint quality.

Introduction

The method proposed, while applicable to various types of cellulose fibers, was developed by experimentation with cottonseed linters, primarily "second-cut"