TABLE IV
Relative Whitening Effect

Brightener	I	II	III	IV	V
Untreated cotton	100	100	100	100	100
Triazone	59	49	42	74	76
Triazone (½ of load untreated cotton	38	27	25	56	58

I—Triazinylstilbene, II—Triazinylstilbene, III—Benzidenesulfone, IV—Naphthotriazole, V—Bisbenzimidazole.

The main reason why brighteners give weaker results on wash-and-wear cotton is that they have less affinity for this chemically modified fiber. With a brightener, such as the triazinyl stilbene type (I), about 25% of the initial brightener remains in the detergent bath after the washing cycle, and approximately 25% is removed from the triazone resin-treated fabric in the rinse cycle. Upon sequential washing, the amount left behind becomes progressively greater. What also contributes to the reduced effect is the fact that most wash-and-wear cotton absorbs more UV radiation than does untreated cotton. In addition, wash-and-wear contains less moisture. At 65% R. H. and 70°F. resin-treated cotton contains about 25% less moisture than untreated cotton. Most brighteners fluoresce less strongly as the moisture content of the fabric is reduced.

We have seen that with most of the wash-and-wear finished cotton the current optical bleaches give a substantially reduced initial effect. This effect is reduced even further when the fabric is exposed to sunlight. The loss of fluorescent intensity of most brightener-treated resin-finished cottons is 25% to 30% greater than brightener-treated cotton without the wash-and-wear finish. Another fastness property to consider is hypochlorite fastness. Those brighteners which have good hypochlorite fastness on untreated cotton still have good hypochlorite fastness on resin-treated cotton. Those brighteners that are poor in hypochlorite fastness on untreated cotton are poorer still on resin-treated cotton, especially when bleach is added early in the washing cycle. The reason for this reduced effect is that the brightener exhausts more slowly onto wash-and-wear cotton, therefore there is more time for it to be attacked by bleach before it attaches itself to the fiber. Once on the fiber, the brightener has reasonably good fastness to bleach.

All of the resin-treated fabrics used in gathering these data were prepared under controlled conditions in our Textile Chemicals Laboratory. The brightener effect on commercial wash-and-wear cotton could differ somewhat from our results. Factors that might cause differences are the amount of resin solids applied, type of catalyst used, curing time and temperature, and such additives as softeners, lubricants, and hand modifiers.

Summary

More than 50% of certain classes of wearing apparel, such as men's shirts, currently being sold are made of wash-and-wear fabric. This percentage is expected to increase even more in the future.

The reaction products used in preparing wash-and-wear cotton and the proposed mechanism whereby these products modify cotton have been described.

Data have been presented to show the reduced whitening effect and fastness properties obtained with the current optical bleaches on wash-and-wear cotton as compared with untreated cotton.

Acknowledgment

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REFERENCES

1. Allen, E., Am. Dyestuff Reporter, *46*, No. 12, 425–432, June 17, 1957.
2. A Daily News Record presentation, based on newly available data from National Cotton Council, E. I. du Pont de Nemours (for all synthetic fibers), and U. S. Department of Commerce, June 1959.
3. Cameron, W. G., and Morton, T. H., J. Soc. Dyers Colourists, *64*, 329 (1948).
4. Cooke, T. F., Dusenbury, J. H., Kienle, R. H., and Lineken, E. E., Textile Research Journal, *24*, No. 12 (1954).
5. Gagliardi, D. D., and Gruntfest, I. J., Textile Research Journal, *20*, 180 (1950).
6. Cooke, T. F., Roth, P. B., Salsbury, J. M., Switlyk, G., and van Loo, W. J., Textile Research Journal, *27*, 150 (1957).

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A Report on the Problem of Residual Solvent in Solvent-Extracted Meals[1]

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SOLVENT-EXTRACTION METHODS are used for at least 90% of the soybeans and 30% of the cottonseed processed in the United States. Solvent processes are also used on flaxseed, safflower seed, rice bran, and others. Because the process yields quality products at a high extraction efficiency and can be operated continuously and economically in medium-to-large installations, its use is expected to expand further.

The solvent generally used is commercial normal hexane with boiling range of 152°F. to 157°F. The industry is well aware of the flammable nature of this solvent. Operators of solvent-extraction plants have adopted stringent procedures and regulations to guard personnel and property against the hazards of fire and explosion.

The lower explosive limit (1) (LEL) of hexane is 1.2% of solvent vapors in air by volume, and the upper explosive limit (UEL) is 6.9%. Such explosive mixtures of solvent vapors and air may occur from a number of causes, such as spills, leaking gaskets, stuffing boxes and seals, incorrect venting, inadequate con-

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densing capacity, inadequate cooling water, and high residual solvent content of the oil and meal products. All of these are carefully controlled in a well-operated plant. The last two items however are greatly affected by the quality of the operations in the plant, and the operator should know if the solvent content of the oil and/or meal product is at a safe value.

In the case of the oil, the closed cup flash-point test furnishes a satisfactory indication of oil desolventization. This has been incorporated in the trading rules (3). On the other hand, residual solvent in meal in quantities sufficient to produce explosive mixtures with air has been recognized also as an extremely important problem from the beginning of solvent-extraction operations. Although thousands and thousands of tons of solvent-extracted meal have been produced annually, there have been relatively few explosions and fires. But where these have occurred, serious loss of life and property damage have resulted. Therefore a simple and reliable method is needed for detecting the presence of residual solvent when it exceeds safe limits.

Excess residual solvent in meal may be present because of many factors, which include changes in quality or composition of the raw material, rapid changes in the weather, rapid increases in the throughput of the plant, fluctuating steam pressure, faulty or incorrect operation of desolventizing equipment, etc.

Plant operators, in general, expect to get the maximum production through the plant. This can only be done safely if the effects of changes in throughput can be checked by actual measurements. The determination of residual solvent in meals thus is seen to be a very important test.

Methods Now Being Used

The methods currently used by the industry for determining residual solvent in meal can best be reviewed by summarizing the findings of the A.O.C.S. subcommittee on residual solvent in meals. One of the authors (Ross Brian), who is a member of that committee, sent a questionnaire to 83 solvent-extraction operators. Forty-three replies were received, of which 23 indicated that they used a method for determining residual solvent in meal and 20 stated they did not use a method. Of the 23 only three used a quantitative method; the other 20 used qualitative methods. Eight indicated that the method they used was satisfactory. The general consensus is however that a more satisfactory method is required.

There were two qualitative methods in general use. a) A sample of the extracted meal is placed in a tightly covered metal can. Size of cans, methods for mixing the contents, and time and temperature of equilibration varied appreciably. The lid is partially lifted, and a small flame is inserted into the top of the can. If a pop or flash results, it is obvious that the residual solvent is too high. b) In the second method a combustible gas detector, such as the MSA (Mine Safety Appliance), is used for sampling the atmosphere within a conveyor continuously or for sampling the atmosphere within a jar containing a sample. Several arrangements of the MSA in conveyors are used. The alarm is generally set to sound when the concentration reaches 40% of the lower explosive limit. The main difficulty appears to be clogging of the intake on account of the dusty and humid conditions of the atmosphere within the conveyor.

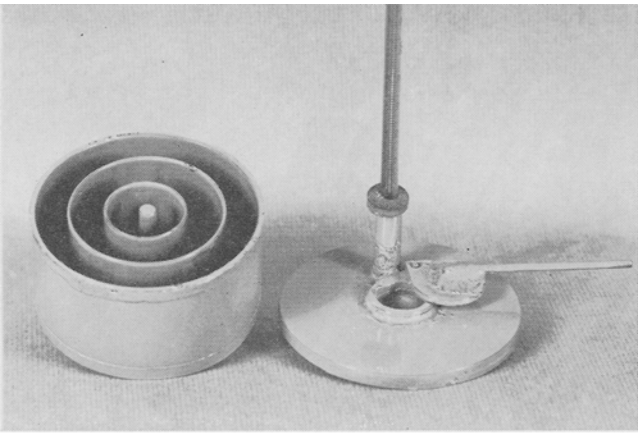

FIG. 1. Copper-cup flash-tester for meal.

Three quantitative methods were reported. a) Moisture is first obtained by toluene distillation, then moisture and volatile by the oven method. The difference is recorded as percentage of hexane. This method is time-consuming, and the accuracy obtained has not been fully determined. b) Nitrogen is passed through a pint sample at 150°F., then dried in two columns; the hexane is absorbed on activated carbon. The activated carbon is weighed to determine the amount of hexane absorbed. c) Another possibility is azeotropic distillation methods.

A method using gas chromatography has been investigated by at least one person, but it does not appear too attractive for mill use because of the cost of equipment and the need for a specially trained operator. A practical method for use in solvent-extraction plants has reportedly been developed by Paul Van Der Voort, of Anvers, Belgium. But to our knowledge he has not as yet published the method.

There are several methods based primarily on analytical procedures that could possibly be investigated as methods of determining both quantitatively and qualitatively residual solvents in meals. Some examples are: a) electrical detectors; b) adsorption methods which include such adsorption media as silica gel and activated carbon; and c) physical-chemical methods, such as use of gas interferometer, conductivity methods, absorption of radiant energy, and vapor pressure.

Requirements of a Method

The methods should detect percentages of solvent in meal that are potentially dangerous. This is undoubtedly the theory upon which the closed-can, "pop" test is based. There should be no question in any observer's mind that a meal which flashes or "pops" is potentially dangerous. Thus, if the conditions under which a flash or "pop" is obtained are more conducive to the liberation of traces of solvent than the least favorable large-scale storage or handling conditions, there should then be confidence in the test. A flash would then indicate an unsafe meal and no-flash a safe meal.

Preliminary investigations by members of the subcommittee on residual solvent in solvent-extracted meals are showing progress.

Recent Test Methods Investigated

James K. Sikes, Plains Cooperative Oil Mill, Lubbock, Tex., a member of the subcommittee, has reported on the use of a modified Pensky-Martens closed-cup flash-point testing apparatus for testing meal samples (2). Briefly, this method detects solvent percentages as low as 0.05% by weight. Close agreement between duplicates was found if proper caution was exercised. The method yields a quantitative estimation in that the lowest flash-point temperature is related to the solvent percentage.

A method was studied which uses a copper cup about 3 in. in diameter and $1\frac{1}{2}$ in. deep (Figure 1). Concentric rings made of copper tubing 2 in. and 1 in. in diameter, respectively, and a rod $\frac{1}{4}$ in. in diameter at the center (all $1\frac{1}{2}$ in. high) furnish conducting surfaces for uniform heating of the meal sample under test. Because of the excellent heat conductivity of copper the temperature gradient between various parts of the cup is small, and no portion of the meal sample is more than $\frac{1}{4}$ *in. away from a heating surface.* The cover is made of brass, fitted with an opening for a thermometer and a sliding disc which can be moved horizontally to uncover a hole $\frac{5}{8}$ in. in diameter, across which a small test flame may be passed. A gasket, $\frac{1}{16}$ in. thick which makes a seal with the outer ring of the cup, also provides a space for solvent from the several annular spaces in the cup to reach the center hole. The cup holds about 87 g. of meal for each test.

Meal samples are prepared by pipetting hexane into a 16 oz. jar, into which part of a 200-g. sample of solvent-free meal has been placed. The rest of the meal sample to total 200 g. is then added; the jar is tightly closed, shaken, and allowed to equilibrate for 1 hr. at room temperature. The jar is then placed in the freezing compartment of a household refrigerator for at least 1 hr., along with the test cup. The cottonseed meal used contained 0.85% lipides and 6.2% H_2O.

To carry out the test, the cup is removed from the refrigerator, wiped dry, completely filled with meal, and closed with the cover. The thermometer is inserted so that the bulb is centered in the meal between 1-in. and 2-in. rings. The only air space is that formed by the $\frac{5}{8}$-in.-in-diameter hole in the cover, which is $\frac{1}{8}$ in. thick.

The cup is placed on two layers of asbestos wire gauze which, in turn, rest on a hot plate which has been operating continuously at low heat. The rate of temperature rise is about 10°F. per minute. The test is discontinued at 200°F. The cover disc is moved aside, and the test flame is applied about every 60 seconds. "Pops" or flashes are obtained over a range of temperatures to indicate the presence of solvent.

Experimental Results

The initial temperatures at which "pops" or flashes were obtained for various hexane percentages are shown by the solid curve in Figure 2. The lowest hexane percentage yielding positive results was 0.04%, but in some instances "pops" or flashes were obtained at 0.03%. The initial temperatures at which flashes were obtained by Sikes (2) are shown by the dashed curve in Figure 2. These values are about 30°F. higher than those reported but were not obtained below 0.05%.

For comparative purposes 1,500 g. of meal with the calculated volume of hexane were placed in a No. 10 size friction top can. The meal filled the can to within 1 in. of the cover. A No. $6\frac{1}{2}$ rubber stopper was fitted tightly into a smooth round hole in the cover. By removing the stopper and applying a flame, vigorous flashes were obtained for hexane percentages as low as 0.04% after keeping the cans at room temperature for 1, 4, and 6 hrs. and only very slight flashes after 24 hrs. No flashes were obtained below 0.04% hexane.

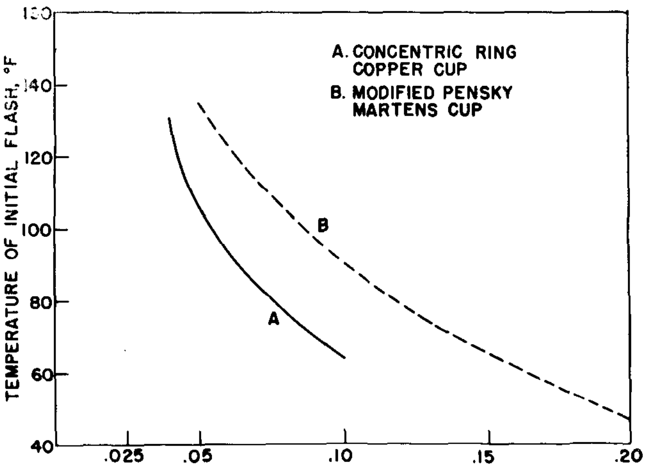

FIG. 2. Relationship between hexane percentage in meal and initial flash.

Discussion

It is believed that the test conditions used with the concentric ring copper cup are considerably more severe than those likely to be attained in commercial operations. The heating cycle should be more conducive to detecting solvent than the room temperature conditions in the closed can methods. The copper cup method yields some quantitative estimate of the solvent percentage present.

For testing mill samples the copper cup could probably be used without equilibrating or refrigerating the sample to get a quick indication. With refrigerating more time would be required, but quantitative information might result.

In using the closed can test for mill samples, one or two hours of equilibrating time would probably be needed. At the Eighth Cottonseed Processing Clinic it was shown that if all of the solvent in a box car at 2,600-cu.-ft. volume, containing 80,000 lbs. of meal, were volatilized and evenly diffused throughout the air space with no loss of hexane to the outside, the lower explosive limit would be reached with 0.0061% hexane in meal and the upper explosive limit with 0.0349% hexane in meal.

If a standard meal is made up with a definite, low percentage of hexane, is any portion of this small amount of solvent so tightly absorbed by the meal or its lipid content that the "box-car" assumption would not be valid?

Sikes (2) points out that 0.64% solvent in oil yields a flash point at 120°F. His modified closed-cup method requires about 0.07% solvent in meal to get a flash at 120°F. The method described in this paper yields a flash at about 130°F. with 0.04% solvent in meal and occasionally at 0.03%. The meal occupies nearly 100% of the total cup-volume. It should be noted that 0.006% solvent in meal would be equal to 0.6% solvent in the oil if the oil content of the meal is 1% and if all of the solvent had diffused into the oil.

It appears likely that it would be difficult under even severe storage conditions for a solvent content in meal as low as 0.006% to release enough solvent to attain the lower explosive limit in any ordinary confined storage space. This would be due mainly to the "holding power" of the 1% oil content almost certain to be present. The failure to obtain flashes at the lower solvent percentages is probably due in part to absorption of hexane in the oil content of the meal.

This method is believed to provide test conditions considerably more severe than those likely to be attained in commercial operations.

The apparatus required is simple, and it should be possible to fabricate it in most small machine shops. The method is not elaborate and with careful operation should yield reliable and duplicable results. The preliminary results indicate that it may be sufficiently sensitive.

Recommendations

It is recommended that this method be tried by other members of the subcommittee and by any others in the industry who are interested. The results obtained should then be subject to rigorous analysis to determine whether the method has sufficient merit to be considered for plant control purposes.

A drawing of the concentric ring copper cup tester will be made available on request to those interested in constructing a cup for experimental or control purposes.

Summary

The hazards of excess residual solvent in solvent-extracted meals and methods currently used for its measurement are discussed. Preliminary results are reported with a simple copper-cup flash-tester with concentric rings as heating surfaces. Solvent contents as low as 0.03% can be detected. The method is semiquantitative. The method may be useful for plant control purposes.

REFERENCES

1. Perry's Chemical Engineers' Handbook, p. 1868.
2. James K. Sikes, J. Am. Oil Chemists' Soc., 37, 84 (1960).
3. Trading Rules, National Cottonseed Products Association, 1959–1960, p. 67, rule 151.

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Continuous Refining of Crude Coconut Oil in a Pressure System[1]

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Refining of crude vegetable oils has progressed from the art of kettle refining as practiced 25 years ago to the science of modern continuous centrifugal processing. This statement is commonly accepted for such oils as soybean, cottonseed, peanut, and corn. However when we discuss the short-chain lauric acid oils (1) such as coconut, babassu, and palm kernel, we find the general practice is still to use the antiquated kettle method.

A study of these lauric acid oils indicates that they are readily saponified when processed in the earlier type of standard continuous caustic soda process with its comparatively long mixing contact time of oil with lye. The high excess of caustic soda over the stoichiometric amounts, as used in conventional refining, leads to large amounts of saponification. These factors in the phase system oil-soap-water, and oftentimes the added factor of entrained air when using open discharge centrifugals, tend to form stable emulsions which defy efficient separation even under the high gravitational field of centrifugal force.

With the development of the all-Hermetic continuous refining process (2, 3) the problem of air entrainment during separation was eliminated. After much intensive research the other factors, such as reagent concentration, temperature, and mixing, were determined and now may be specifically controlled to give a high quality of refined oil and at the same time a high refining yield.

Theoretical Background

After considerable study of the basic problem the McBain (4, 5) phase diagrams for aqueous soap systems were selected as a starting point. For purposes of illustration, Figure 1 shows in part the phase behavior of sodium laurate, electrolyte, and water at 90°C. (6). This system with weight percentage of anhydrous soap (sodium laurate) as the ordinate and weight percentage of electrolyte as the abscissa is divided into various phase areas.

For background information the diagram will first be described before showing its relationship to the

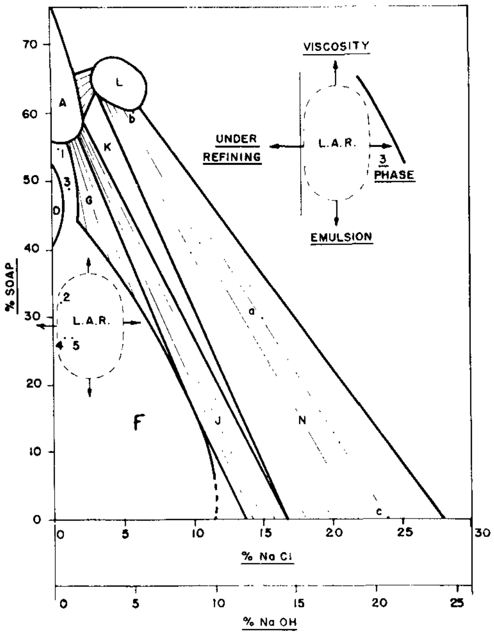

Fig. 1. Sodium laurate at 90°C.

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