both straight clarification and clarification with 5% water, in an effort to substantially reduce the phosphatide and unsaponifiable fractions. Table IV gives the results of this test.

The data in Table IV indicate that neither straight centrifugal clarification, nor clarification with 5% water, is completely effective in removing the acetone-insoluble or unsaponifiable fractions from the oil and that the loss of oil is significant in both cases.

Because the oil could not be satisfactorily neutralized without excessive oil loss in separating the soap stock, no bleaching or steam deodorization tests were run.

## Discussion of Results

Possible uses for this oil appeared to be splitting and distillation to recover the various fatty acids and glycerin, and splitting for use as a soap stock. Edible oil uses are ruled out because of difficulties in refining the oil.

As a source of fatty acids, because of the high unsaponifiable fraction (3.5 to 5.5%) and dark color, this oil would be classified with vegetable oil foots. As a soap stock the oil does not appear promising because of the high unsaponifiable fraction and dark color. No investigation has been made of what applications, if any, the unsaponifiable and acetone-insoluble fractions may have.

## Conclusion

The oil extracted from dried brewers' grains from a brewery using rice as an adjunct is somewhat similar in its fatty acid composition to cottonseed oil, but its dark color, high free fatty acid (19.6 to 23.2%), high unsaponifiable fraction (3.5 to 5.5%), and high acetone-insoluble fraction (2.11 to 9.23%) lessen the value of this oil. Since conventional methods of refining did not prove satisfactory, this oil appears to be of value only as a source of fatty acids and would therefore have to be classified with vegetable oil foots.

## Acknowledgments

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# The Production and Standardization of a Detergent Soil[1]

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A STANDARD is a defined measure of quantity, value, or quality, or by general consent is an example or test. One of the difficult parts of any standard is attainment of the general consent. A standard must possess some degree of reproducibility, and this factor is one of the reasons for delay in the acceptance of "standard" soils or soiled fabrics. High standards are not easy to attain, and such materials as common chemicals must be subjected to considerable purification and subsequent analysis before they become recognized as standards. Evidence of lack of analytical or statistical control of soils is one of the deficiencies to be noted in much data published on this subject.

One of the main reasons for lack of an accepted standard soil or soiled fabric is feeling that the laboratory soiled fabrics and washing methods show little or no correlation with actual practice. However the need for an artificially soiled fabric which could serve to screen the literally thousands of synthetic detergents or their multitudinous combinations with each other and with other detergent aids is readily understood. From the tone of publications on detergency, the methods of washing and the so-called standard soils appear to be the result of the then rather recent research. No indication is given as to their suitability over prolonged periods of usage. Standardization of soil by preliminary tests seems to be the exception rather than the rule, and of the many papers published few provide such necessary data (5). A notable exception to this generalization is the published information on recently available power-laundry soiled fabric (3). This paper is presented to give the results of 12 years continued experience with one type of soiled fabric and records the many variables which must be controlled to standardize it.

Soil has been aptly described as matter out of place, and this description adequately covers the multitude of materials which it is expected a detergent will aid in removing. To limit the discussion, the removal of soil in this instance is confined to removal from textile fabrics, but even then the affinity of soiling materials for various fibers presents a complicated picture, to say the least. As a further limit, since it represents a large proportion of the garments repeatedly and frequently washed, cotton will be the fiber discussed.

Investigation of the effects of the various individual soils and their further complex mixtures upon cotton could be the work of a lifetime. However a

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more immediate answer is generally required by industry, and a composition and technique designed to ascertain speedily the quality of materials has generally proved successful. Certainty as to the validity of this type of test is generally ascertained by supplemental practical trial.

*Requirements of a Standard Soil.* The minimal requirements for a standard soil are that it

1. Should be reproducible and quantitative,
2. Should show removal from the fabric base to an extent comparable with removal of natural soils during practical washing procedure, and
3. Should provide an absolute rather than a comparative value.

Differently expressed, the laboratory requirements for a standard soiled fabric are more specific:

1. The fabric should be of uniform characteristics.
2. The soiling operation should provide the same initial amount of soil, and the same removal value for any given detergent under identical conditions of cleansing.
3. The soil removal values should be reproducible, preferably of analytical accuracy.
4. The effect of aging should be minimized.
5. The method for determination of soil removal or retention should be reproducible and preferably quickly accomplished.

These are the goals which should be met by standard soiled fabrics, but seldom are they fully achieved.

One of the arguments always advanced in any standard soil meeting is that each specific fiber will require a soil differing from other fibers, but if this were carried to the extreme, then every weave of every fabric or every fiber combination would require its specific soil. This is a practical absurdity, and appraisal of the problem by those willing to work toward a common end ultimately will yield a sound basis for evaluation.

The basis for our own reasoning follows. First, since cotton is the fiber most commonly used and worn and is most frequently washed, this specific field certainly is worthy of investigation. Other cellulosic type fibers are also frequently washed, and their fiber characteristics often make them more easily cleaned than cotton. Second, wool and proteinaceous fibers are perhaps the second most commonly used classification, but in volume of detergent consumed makes the class secondary in commercial value. A standard soil for wool cleansing however is a separate and necessary requirement but will not be dealt with here.

Since there are two main fiber classifications of garments cleansed, though perhaps a number of subsidiary ones, the problem is somewhat narrowed. The weave of fabrics will affect the ease of soil removal, but again a common type of weave may be agreed upon. Others define themselves as specialty cases either comparable or not with the chosen common weave.

This leaves the matter of soil as the further field of discussion. Agreement on this point will be difficult, but on the basis that garments or fabrics may most often be soiled through wear, and these with greasy or oily substances, as well as colored, often water-insoluble matter, a further establishment of understanding should be made. One of the soils most frequently encountered, and very difficult to remove, is the shirt collar or cuff soil. In many cases this almost amounts to a stain, but stains as such are specialty soils, susceptible to specialty removal methods if not removed in the normal process of cleaning. However, a really effective detergent or washing process should result in removal of such soils. The soil then should represent a generally encountered, rather hard-to-remove type, so that a degree of variation between good and poor removal may be discerned. Naturally the soil should be uniform and representative of matter ordinarily encountered, but the ingredients themselves should be readily obtainable in uniform quality and easy to apply. The materials which seem most nearly to meet these requirements are carbon and animal, vegetable, or mineral oils, since they are often encountered and are most generally used for the purpose. Because they lend themselves to chemical analysis, various pigments as represented by manganese dioxide or black iron oxide have been used rather than carbon.

Should agreement in principle to this point be reached, the next hurdle is the means for estimating soil removal. In general there are two approaches, either by absolute or by comparative measure. In practical experience a fabric is clean when, by comparison, the surface closely approaches the appearance (or reflectance) of a piece not previously soiled. This may be considered an absolute measure in that all the quality characteristics are susceptible to investigation but is not necessarily quantitative from an absolute viewpoint. A good soil would permit measurement of soil removal over the 0-100% range in exact scale. However soils chosen with this specific purpose in mind often are decidedly artificial since they seldom or never are encountered in practice. The question which must then be resolved is whether soil used for either absolute or reflectance measurement is removed by the same mechanism as natural soil.

Since visual observation of cleanliness is relied upon practically to determine effectiveness, it is not unusual that reflectance methods have been most generally employed. The apparently inherent difficulty with the reflectance method is that a rearrangement of the soil occurs at the fiber-fabric surface, a relatively small amount of pigment resulting in a marked reduction in reflectance out of proportion to the actual amount retained. *But this likewise occurs with natural soils.* Cleanliness has not been attained so long as the surface appears darkened, no matter what relatively large proportion of the soil has been removed.

Although no indication generally is given in the many papers which are published, it is apparent from many of them that they are the immediate product of considerable research effort, but that they have not been time-tested. Because we have had many years of experience with the same general soiled fabric and because our experience may be of assistance to others, we present our method of operation in soil preparation and standardization.

The process may be subdivided as follows, and each section will be dealt with separately:

1. Fabric
2. Desizing of fabric
3. Soil
4. Soiling machine
5. Wash test machine
6. Wash test method
7. Storage
8. Evaluation of washed swatches
9. Soiled fabric testing
10. Statistical data
11. Control chart data
12. Application to practice.

1. *Fabric Choice.* Indianhead fabric was chosen from a number tested because it was available in quantity and uniform in quality, had the proper texture, and seemed to permit greater differentiation in soil removal with a given detergent and soil than did other weaves. Other similar type weaves, generally of finer yarn size, have been used. Indianhead fabric is a plain weave sheeting, has a thread count of 48 x 54, is available in several widths, and has a weight of 5 ounces to the square yard. To minimize our desizing problem we purchase on specification from the manufacturer a scoured, bleached, dried, but unmercerized or otherwise finished grade.

2. *Desizing.* Early experience indicated that sizing agents should be removed, and this was accomplished at first by treatment in a cycle of acid, caustic, and soap baths. For fabrics containing starch, desizing enzymes have been used, but this never was done under our procedure. Other investigators simply use the fabric as received and apply the soil over any sizing agent present.

We believed that for purposes of uniformity all sizing should be removed. Variation in fabric characteristics resulting from small scale operation led to desizing in a 25 x 25″ pony wash wheel, eliminating the acid treatment. This step was simplified by obtaining Indianhead fabric bleached and scoured but not further treated. This meant that chemical change or deposition of chemicals liable to change the surface reactivity of the fabric were eliminated since a mercerized or chemically treated surface is much more reactive than one not so treated. The desizing operation follows:

*Equipment.* A 25 x 25″ pony wash wheel, with a capacity of 25 pounds dry weight, is used for the desizing operation. If smaller amounts of fabric are to be desized, care should be exercised to maintain the ratios between fabric, water, caustic, and soap.

If desizing is done in an open vessel, such as a beaker, care should be taken to keep the fabric under the surface of the solution at all times since otherwise surface defects resulting from chemical degradation will occur.

*Operation.* Softened or distilled water is used.

*Load.* The load consists of four strips of fabric 45 feet long by 36 inches in width. This weighs approximately 18 pounds.

*Caustic Scour.* Operated at 4 inches (14 gallons) of water in the running wheel. This approximates 0.8 gallons per pound of fabric. Four hundred and thirty grams of sodium hydroxide, C.P., are dissolved in a small volume of water, then added to the wheel when the temperature has approached the boil (this represents a concentration of 0.8%). The boiling operation is continued for 30 minutes with the wheel in constant operation. Drop the bath at the end of this period.

*Rinse.* Run three inches of water at 160°F. into the machine (12 gallons) and operate for five minutes. Drop the rinse.

*Soap Scour.* Run four inches of hot water into the wheel, add 40 grams of a neutral soap flake and bring to the boil. Run 10 minutes at the boil. Drop.

*Rinsing Schedule.*

a) 4 inches water at 160°F.
b) 6 inches water (19 gallons) at 140°F.
c) 6 inches water at 120°F.
d) 6 inches water at 100°F.

Check rinse water at this point by titration to methyl orange endpoint, comparing results with a blank of the water in use. If soap is still retained, repeat rinsing until the titration value for the water used is attained. Last rinse. Six-inch height of distilled water. Extract.

*Finishing.* The lengths of fabric are ironed dry at a plate temperature of 370°F. on a flat plate ironer (to reduce lengthwise distortion). The 45-foot ironed strips are cut lengthwise in 6¼-inch width strips.

3. *Soil.* A test soil generally will comprise a binding agent and a material which permits quantitatively estimating removal and which in itself may be a natural soil. Since soot is a common soiling agent and certainly lends itself to reflectance measurement against a white fabric, it is not unusual that carbon in some form should be used. Carbon will vary widely in composition depending upon its method of manufacture. Some may be very finely divided, others coarse, and the particle size distribution may vary widely. Some carbons may be predominantly oil-dispersible and others water-dispersible, but apparently satisfactory results have been obtained using either type.

We have used Oildag Concentrate satisfactorily for at least 12 years. Oildag is comprised of colloidal graphite and apparently an oil soluble dispersing agent, dispersed in mineral oil. This forms relatively stable dispersions in nonaqueous solvents. So long as the code number which appears on the Oildag bottle is specified, satisfactory reproducibility by the manufacturer has been noted. The binding agent for the graphite may be chosen from a wide variety of agents, but we prefer a vegetable oil and have used Wesson oil, though Mazola oil can be substituted for it. Others have used lard, tallow, or other natural oils. Yet others have used mineral oils because they are not readily susceptible to atmospheric oxidation. We chose Wesson oil because when it was properly aged or cured on the fabric, it made the graphite much more difficult to remove than did mineral oil, giving a satisfactory spread in soil removal. The difficulty in the use of an oxidizable oil however is that the degree of oxidation must be controlled and the storage conditions maintained at an optimum to prevent further oxidation.

The medium to be used for dispersion of the carbon and oil is obviously important. In some systems graphite or carbon is deposited upon the fabric in water, loose carbon removed, and the soiled fabric either used as such or the dried fabric impregnated additionally with an oil. Water is a safe and inexpensive medium for soil application, but the fabric must be treated to remove wrinkles and loose carbon. Choice of a chlorinated solvent may be preferable to a naphtha solvent wherever fire hazard is involved, though the latter is less expensive and relatively nontoxic.

A technical grade of carbon tetrachloride has been used for years, and while we have no evidence that inhibitors added to the carbon tetrachloride may affect oxidation, this is a possibility which has not been explored.

The soiling solution which we use has the following composition:

5.0 grams Wesson oil.
10.0 grams Oildag Concentrate (Acheson Colloids Corp.).
12.0 liters carbon tetrachloride (Dowclene, Dow Chem. Co.).

The amounts of Wesson Oil and Oildag are weighed to the accuracy indicated, and the carbon tetrachloride measured from a two-liter graduate. Care is taken to disperse the Wesson Oil and Oildag thoroughly during dilution. Each batch of soil solution is prepared immediately prior to use and is sufficient for one 45-foot roll of fabric.

4. *Soiling Machine.* The soiling operation is important, and to insure reproducibility of application it is general practice to use a machine of some sort. One of the mechanically operated implements of this kind

was described by Van Zile (4). Previous discussion concerned the choice of medium for dispersion of the soiling agents. Since the soils used are generally water-insoluble, either water or some more volatile solvent may be used as the dispersing medium. Generally a chlorinated solvent or hydrocarbon is used as a means for uniformly applying them to the fabric.

Our machine was developed from an initially hand operated heated tube to the present equipment. Since moisture as dew deposited on the fabric (as a result of solvent volatilization) has such a marked effect upon soil characteristics, the machine was designed to minimize the effect of condensed moisture by raising the dewpoint.

The machine is shown in Figures 1, 2, and 3. The soiling box in Figure 1 is constructed with five alternating rods evenly spaced over the length and from 1 to 2 inches from the bottom of the pan. This holds the fabric in an over and under position while it is passed through the soiling bath. The fabric does not require squeezing to remove excess soiling solution and simply passes over the metal roll into the heating chamber. Figure 3 shows the winding device operated by a fractional horsepower motor operated to give a linear fabric speed of 9 feet per minute. The large fan at the bottom of this figure produces the concurrent air flow in the machine. An air velocity of from 900 to 1,000 feet per minute is maintained; the cold air passes over a series of Koilfin heaters in the lower chamber of the machine and emerges from the heating chamber into the drying chamber at the point where the wet soiled fabric is entered.

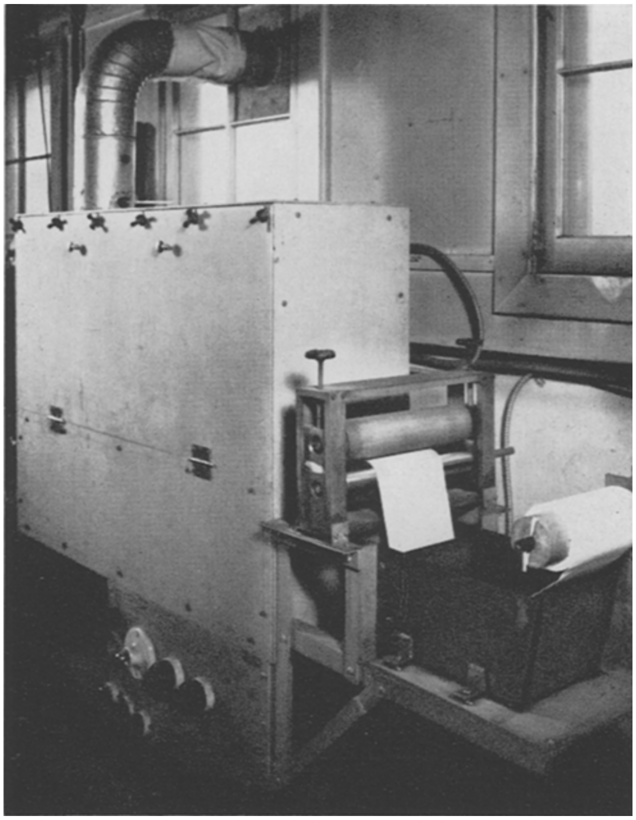

FIG. 1. Fabric entering soil box and passing over roll into drying chamber.

The temperature is thermostatically maintained at the inlet to the drying chamber at 35-37°C. Four passes through the machine give the depth of soil required, and the fabric is reversed from side to side with each pass. By suitably increasing the soil concentration this might be reduced to two passes, but we hesitate at the moment to initiate this variation since so much effort has already gone into the present procedure and it is not likely to be improved by such change.

The essentials of the operation follow:

*Machine Conditions.* Temperature 35-37°C. Air velocity 900-1,000 feet per minute (Alnor Velometer with jet number 2425-18 for measurement). Fabric passage rate of 9 feet per minute.

*Soiling Operation.* A leader of fabric 1½ inches wide by 24 feet long is wound into the recessed slot on both winding spools (see Figs. 1 and 3). A 45-foot length of desized 6¼-inch width fabric is transferred to one of the spools, and this tacked to the leader from the winding spool.

The soiling solution is shaken well and transferred to the soiling box covering the upper rods by a 2-inch depth. With the machine in operating condition, the soiling operation is begun. Four passes through the soiling solution are made for the roll of fabric. The fabric is turned each time after passage so that the side first down is up on the second pass, and so on.

Upon completion of the four passes the roll is properly identified, then transferred at once to an airtight container, and stored in a mechanical refrigerator, awaiting the first step of standardization.

The soiling solution is discarded and fresh solution used for each of the rolls soiled.

5. *Wash Test Machine.* Of the several requisites for a machine in which to perform the washing operation perhaps the most important are:

1. Temperature and the mechanics of the washing action should be reproducible,
2. Operation should be simple and a large number of replicate samples should be processed simultaneously,
3. The machine should exactly duplicate some commercial operation, or the washing results should be readily translated to other washing conditions.

The mechanical work involved has marked bearing upon the effectiveness of soil removal as indicated by the work of Bacon and Smith (2).

Many machines have been developed for the purpose of controlling the mechanics of the washing operation. The Launderometer (Atlas Electric Devices Company, Chicago) has been widely used for many years for this purpose. Others have attempted to duplicate some specific type of washing action, and the most recent of this type is the Terg-O-Tometer (Baker Iustrument Company, Orange, N. J.). Generally, however, instruments other than the afore-

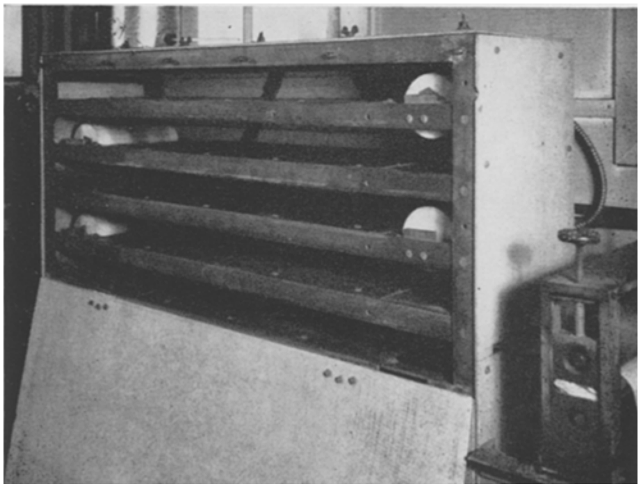

FIG. 2. Interior of drying oven. Direction of fabric from right to left and from bottom upward.

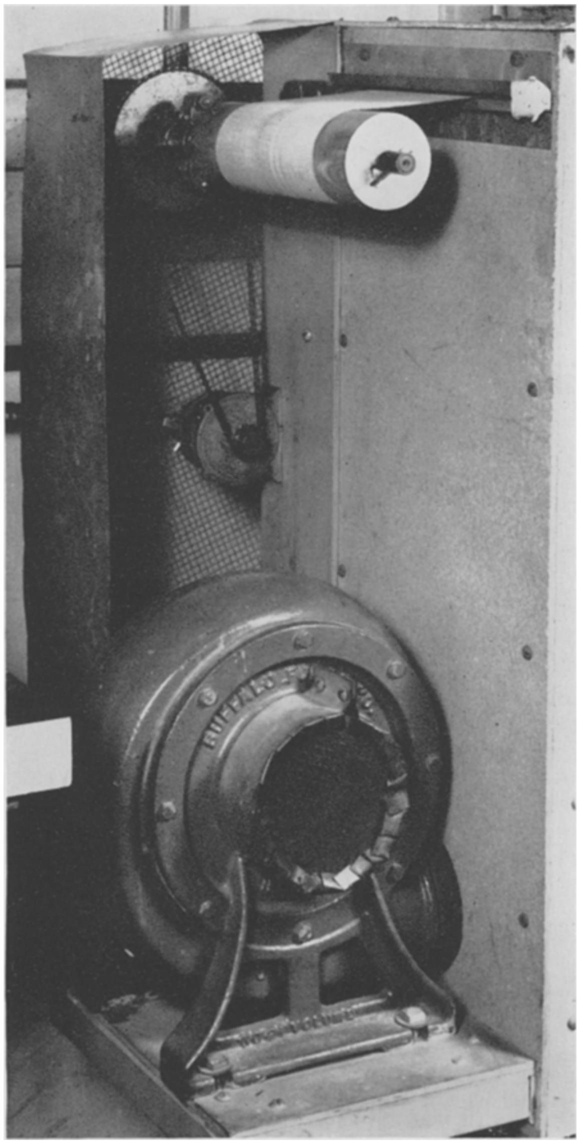

Fig. 3. Fabric winding mechanism (above) and blower.

mentioned have proved costly to produce and costly to operate because so few tests can be made per day. We hold no brief for any of the machines, having used both of the foregoing as well as full or partial scale home washers or power-laundry wheels. Wherever a relatively large number of tests can be made simultaneously and under good control, costs of operation are reduced and testing speed increased.

6. *Wash Test Method.* Another variable in operation which must be resolved is the actual washing procedure. Ordinary washing in the home may be of the single wash, single or double rinse type. In the power-laundry the multiple suds, multiple rinse principle is followed. Both methods have been described in the literature. We prefer, and have used the multiple wash system in the laboratory, followed by a double hand rinse, by squeezing in fresh water of the hardness required. There may be objections to this method in that it does not duplicate practical operation, but excellent results have been obtained with it nevertheless. The method of operation follows:

*Swatches.* Five-inch lengths are cut from the 45-foot roll of soiled fabric. Duplicate swatches are used for each detergent and for each water hardness.

*Wash Conditions.*

1. Volume of solution—100 ml.
2. Rubber balls—10 (standard for Launderometer).
3. Single swatch per pint jar.
4. Temperature—140°F., attained by preheating of solution and use of a loading table.
5. Concentration—ordinarily 0.2% though a range of concentrations may be used.
6. Water hardness—50 and 300 ppm. as $CaCO_3$ (see comments below).
7. Number of washes—4.
8. Time per wash—10 minutes.
9. Rinse twice, by hand, in water of hardness used in wash test.

*Scheme of Test.*

1. Wash the 5 x 6¼-inch swatch 10 minutes. Dump the solution, swatch, and rubber balls into a wire drain. Squeeze swatch lightly by hand to remove excess solution.
2. Remove a 1½-inch strip from the 6¼-inch dimension of the swatch.
3. Rinse the 1½-inch duplicate strips lightly by hand by squeezing in water of the hardness being used.
4. Transfer the remainder of the larger swatches to fresh solution pretreated as before and wash for another 10 minutes.
5. Repeat 1, 2, and 3 until there are available from the duplicate swatches eight 1½ x 5-inch smaller strips. See Fig. 4.

*Drying of Washed Swatches.* Migration of pigment can occur when the washed swatches are slowly dried at room temperature. This should be obviated by any means which does not affect the reflectance of the washed fabric.

*Drying.* The washed and rinsed swatches are arranged in order on a sufficiently large aluminum sheet and immediately following the fourth wash, the sheet is transferred to the oven used to cure the soiled test fabric. The temperature is controlled at 65 plus or minue 2°C. and as soon as the swatches are dry, they are removed from the oven and stored overnight under room conditions prior to making reflectance readings.

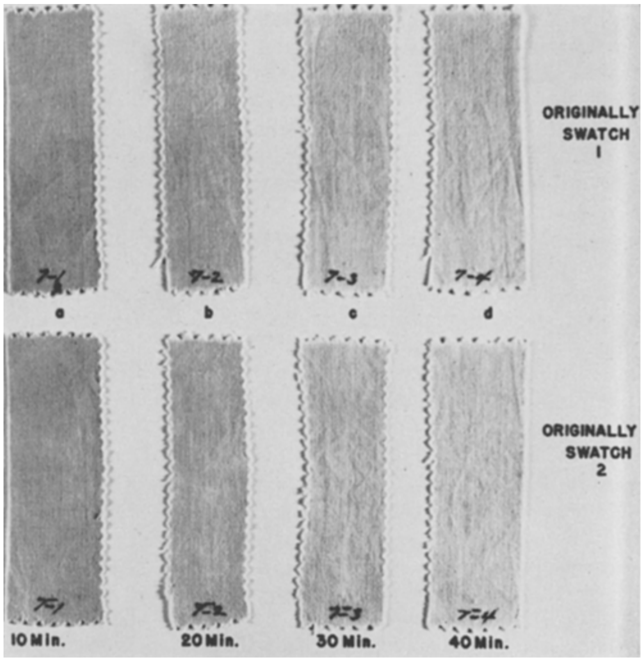

Fig. 4. Washed pieces from the four 10-minute washes.

In performing the test in this manner there are available data from any one of four swatches at regular time intervals (Fig. 4). These can yield information as to rate and degree of soil removal over a series of washes, or the average value can be used for comparison purposes. When the average value for the eight strips is used this is mathematically equivalent to

$$\frac{2a + 2b + 2c + 2d}{8} = \text{average soil removal}$$

This procedure tends to level out variations which occur as results of unintentional change in procedure, uncontrolled application of mechanical force, and any of the other many variables which plague such operations. One difficulty minimized by this procedure is wrinkle marks (which display greater soil removal at the edges of the wrinkles with resultant difficulty in assay of reflectance).

Some investigators prefer the single wash technic, perhaps because this approximates actual washing conditions, but in so doing they should perform a considerable number of tests. The procedure outlined above is the equivalent of four single washes at different levels of soil retention, which then present a rather different and improved picture of soil removal characteristics.

The water hardness values chosen were for both soft and hard areas in order that detergents might be evaluated for use under the extremes of operating conditions ordinarily found. The water itself is comprised of Ca and Mg salts in the ratio of 60 to 40. There are those who object correctly that many synthetic detergents are more affected by the Ca in the water than by the Mg ions, hence that the ratio of Ca in the water should be increased. Others will criticize the range of water hardnesses chosen. The obvious answer to both criticisms is that a really effective agent will be only mildly affected by either type of water hardness, and that at any rate a full investigation of the characteristics of a material will include concentration-water hardness curves for a range up to 1,000 p.p.m. The present method has successfully served the purpose of screening potential detergents.

7. *Storage.* The ideal soiled test fabric should be completely stable toward aging or storage. Our soil continues to age over a considerable period of time, but to minimize this effect we have found that ordinary mechanical refrigeration while storing of the soiled cloth in a dry atmosphere will prevent change in soil removal characteristics over a period of a month. All of the usual methods for inhibiting oxidation such as vacuum, absence of light, inert atmosphere, desiccator, etc. (and other than the use of an inhibitor) were evaluated in arriving at the most desirable storage conditions noted above.

8. *Evaluation of Washed Swatches.* Previous discussion covered briefly the mechanism for measurement of degree of soil removal. Even though the reflectance method is not absolute, it seems to conform more to the visual evaluation of the washing process. Since the soil is designed to permit a spread of results from original soil to original white (which seldom if ever is attained with these soils), and since this is what the eye sees, regardless of actual weight percentage soil distribution, a photometric method for soil removal evaluation is indicated. Other investigators (5) prefer the measurement of soil removed from the fabric and held in suspension in the solution, essentially disregarding the fabric as a means for evaluation of removal. This latter method utilizes the photometer, reading transmittance against a curve for removal, but possible turbidity of detergent in solution interferes, and somewhat narrows the utility of this method.

A number of suitable photometers are available for measuring reflectance, two of which are the Hunter and the Photovolt. Either can be standardized against magnesium oxide or a working standard. However we prefer, in measuring soil removal, to set the soiled fabric in question at zero on the scale and the white desized fabric before soiling at 100. Removal then is expressed as a percentage of this range. When using the Hunter, the same procedure is, in effect, used when the reflectance of the washed piece is expressed as a percentage of the spread between the soiled fabric and the white fabric. Since some variation in the soiled fabric is expected, as indicated by the primary or secondary detergent standards, these may be used as bases for comparison. The reasoning for this procedure is that the variation may be as much in soiled fabric as in the procedure, and since all samples have gone through exactly the same process (and with the same soiled fabric), variation in the standards, can be arbitrarily applied to the others in the same wash. Whether or not this reasoning is correct, the results obtained using it have been quite satisfactory.

The necessity for a background of constant reflectance (or preferably the use of a sufficient layer of fabric of the same reflectance range) has been mentioned many times in detergent work since the porosity of the fabric will to a degree affect reflectance readings. The use of a battleship gray board with a small, sharp pin at the far surface and another placed on the lower or nearer edge of the board will permit stretching the duplicate swatches, one under the other, for scanning by the photoelectric search unit. Greater thicknesses have shown little or no variation in reflectance readings, and there is obvious advantage to the use of a fabric of the same reflectance range for backing purposes. With the Photovolt the small area search unit is used while with the Hunter Multipurpose Reflectometer the small size of swatch requires a centering device and the insertion of the unit designed for small area determination of reflectance. The procedure for evaluation of swatches follows:

*Reflectance Standards.* Using the small area search unit and the tristimulus filter, set the Photovolt scale at 0 and 100 using the soiled fabric as the zero setting and the original white fabric as 100% reflectance. These swatches are stretched taut in small holders and the instrument is regularly checked against these arbitrary standards during the reflectance readings.

*Swatch Readings.* Using the four-wash duplicate swatches, the two first wash swatches are superimposed, and stretched from the pins on the reading board; the search unit is guided by a small board strip parallel with the washed swatches and spaced from them to center the search unit. The adjustment of the Photovolt is made and the search unit moved slowly up and down the swatch as a mental average of reflectance values is made. The swatches are then interchanged and the average reflectance determined for the second swatch. These two values are recorded, and the same process repeated for the second, third, and fourth wash swatches.

It is unnecessary with this soiled fabric to read both sides of the fabric since periodic checks have shown that variation from side to side of the swatch lies within the accuracy of the reflectance readings.

9. *Soiled Fabric Testing.* Since every load of samples includes at least one standard detergent product, for many years we simply used the soiled fabric as it was cured or artificially aged and without preliminary evaluation. Apparently this is the general method followed by a large proportion of the investigators reporting detergency data.

In an attempt to improve reproducibility we now test each roll of soiled fabric immediately after preparation and without further treatment. There are variations from roll to roll as evidenced through the use of the standard detergent sample. Having ascertained the degree of soil removal immediately after soiling, and knowing the degree of retentivity of soil desired, the freshly produced fabric is then baked in a circulatory oven (Fig. 5) in festooned form for periods of time which experience indicates will provide adequate resistance to removal. After baking, the soiled fabric is again tested under standard conditions to be certain that specified control has been attained.

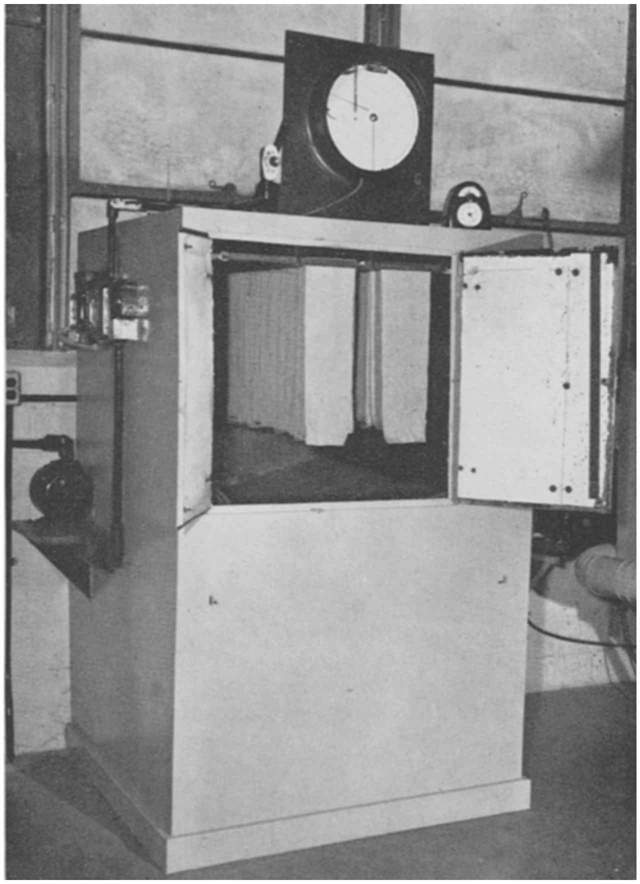

FIG. 5. Curing oven. Air circulated by vanes from left over heating units thence upward and through festooned fabric.

*Procedure.* After soil preparation the fabric is tested under conditions elsewhere specified and with a standard detergent to determine the ease of removal. Based upon the soil removal data, specific curing (or baking) times are given to each roll to secure the desired retentivity. The oven used (Fig. 5) is designed to circulate the heated oven air over thermostatically controlled Finstrip heaters to give a temperature of 65 plus or minus 2°C. The fabric is festooned in the oven to provide maximum uniformity of treatment. After curing, the fabric is again rolled and stored preparatory to retesting to be assured that the soil removal control limits are attained.

When the control limits are attained, the test fabric may be used for evaluation purposes. A storage period of four weeks under the specified conditions shows minor increase in retentivity of soil.

10. *Statistical Data. Wash Test Variability.* The reason for selection of a machine to perform the wash test is a desire uniformly to apply mechanical action to the soiled cloth during the washing operation. Choice of machine is outside the limits of the present discussion. However the Launderometer functions reasonably well to control the variables of temperature and mechanical action and has been used to obtain the test data discussed. Wash test variables other than those introduced by the machine naturally are controlled as closely as possible.

Having attained as close control of the mechanical features of the test as possible, the question then to be answered is what the variation or the reproducibility of the washing process is, using the test fabric in question. Two phases to this question are the reproducibility within one load and the reproducibility from load to load.

Reproducibility within the load may be answered by washing all one Launderometer load with a single detergent under identical conditions of operation. An alternative to this would be to split the load, washing half with one detergent and half with another. This was done with the results shown in Table I. The statistical values given there were developed using the ASTM Manual on Presentation of Data (1). The statistical values were calculated as follows:

TABLE I

Single Launderometer Load. Values as % Soil Removal.

| Test | 50 p.p.m. | | 300 p.p.m. | |
|---|---|---|---|---|
| | Sample A | Sample B | Sample A | Sample B |
| 1 | 28.0 | 41.0 | 33.0 | 35.0 |
| 2 | 32.5 | 37.0 | 33.5 | 36.0 |
| 3 | 33.5 | 40.0 | 32.0 | 36.0 |
| 4 | 32.0 | 39.0 | 28.5 | 35.0 |
| 5 | 30.0 | ...... | 26.5 | ...... |
| Statistical Data | | | | |
| Mean ($\overline{X}$) | 31.2 | 39.3 | 30.7 | 35.5 |
| $\sigma$ | 1.97 | 1.3 | 2.74 | 0.14 |
| R | 5.5 | 4.0 | 7.0 | 1.0 |
| $\sigma_{\overline{X}}$ | 0.98 | 0.75 | 1.37 | 0.08 |

Mean — $\overline{X}$ = the arithmetic mean

Standard deviation — $\sigma$ = the root mean-square deviation about the average

$$\sigma = \sqrt{\frac{\Sigma(X-\overline{X})^2}{n}}$$

Range — R = difference between the smallest and largest observed value

$$\text{Standard error} — \sigma_{\overline{X}} = \frac{\sigma}{\sqrt{n-1}}$$

It is apparent from the data of Table I that one sample in hard water tends to give considerably greater variation than the other, but that in either case the standard deviation is relatively low. With a 95.5% probability ($2\sigma_{\overline{X}}$) it is apparent that these two samples are different with sample B the superior.

Having determined the variability within a single wash series, the next problem is determination of variability of sample data from several different wash loads. Table II presents these data. As would be expected with tests of such duration, there are greater apparent differences between replicate samples than in a single wash. As these data show that variation is inevitable, the next step is to interpret subsequent tests, using the quantitative information available.

In application of data to unknown samples of approximately the same degree of soil removal, the standard error for the standard sample (run in the same wash load) can be applied, assuming that variation in soil and washing conditions can be applied to the test product. In fact, correlation coefficients were developed for a series of two samples tested together over a period of time, and there was direct correlation between the two samples with respect to their variation from test to test.

TABLE II

Multiple Wash Tests. Values as % Soil Removal.

| Statistical Data | 50 p.p.m. | | 300 p.p.m. | |
|---|---|---|---|---|
| | Sample A | Sample B | Sample A | Sample B |
| n | 21 | 21 | 21 | 21 |
| $\overline{X}$ | 40 | 44 | 39 | 40 |
| $\sigma$ | 5.83 | 3.87 | 7.68 | 3.74 |
| Range | 23 | 13 | 27 | 13 |
| $\sigma_{\overline{X}}$ | 1.30 | 0.87 | 1.72 | 0.84 |

In the data given in Table II the standard error ($\sigma_{\bar{x}}$) for sample A is greater than sample B with a value of 1.30 in 50 p.p.m. water and 1.72 in 300 p.p.m. water. A standard technic for utilization of statistical data is to determine the difference between the test sample and the standard, and if this difference is equal to, or greater than twice the larger standard error then the chances are 95.5 out of 100 that the samples are different. As an example, comparison of samples A and B in 50 p.p.m. water in Table II shows that the difference between the mean values is 4 and twice the larger standard error is 2.6. Since the difference is greater than 2.6, the chances are 95.5 out of 100 that the values are really different.

11. *Control Chart Method.* Each series of Launderometer wash tests, for reference and control purposes, contained the detergent used in standardizing the soiled fabric. The data for the standard detergent from each wash test load were recorded and plotted, each dot in Fig. 6 representing a single average value for removal of soil from the test fabric of the period indicated. The control chart values are for six-month periods and exclude the values obtained during standardization. The 1-22 portion of period 1 shows the values obtained with a single batch of standardized soiled fabric.

This method provides a visual check on the effectiveness of control. Every value which falls outside of the control limits should have an explanation if all factors of variation have been controlled and recorded. Following this system, control and adjustment of variables resulted in the narrowed limits exemplified by period 3.

12. *Application to Practice.* The criterion of utility which may be applied to this soiled fabric and wash test method is whether they have consistently resulted in selection of commercially acceptable products. To their credit is the fact that of a large variety of materials which have consistently been shown as effective detergents these have enjoyed sales over the years well into the billions of pounds. Also to their credit is the fact that products claimed as detergents, which the method showed as deficient, have disappeared from the market or have been guided to their proper place in the surface active picture. Certainly it has assisted in our own screening operations, guiding the course of research synthetic work.

The method as a whole has been used successfully to control plant production in addition to routine research evaluation work.

The standard soiled fabric and test method have been used in the commercial development of such products as the Santomerse and Sterox materials, various formulations of them with builders, and the combination of tetrasodium pyrophosphate both with synthetics and soaps.

Since a single soiled fabric does not represent the multitude of soils met in practical washing, the recommended evaluation procedure is to supplement the screening tests with an extended series of practical washing tests using the machines and the actual garments ordinarily encountered. The doubt that always exists concerning soiled test fabric as the sole criterion of quality is whether the garments are cleaned to the high standard desired. Certainly comparative tests can be made in this way, and a high degree of correlation between the screening test and the practical test has been found. There are those who appear to believe that the sole criterion of quality is a comparison of washed garments, but the difficulties inherent in this method are as manifold as in a laboratory screening test. There is no reason why the best features of both tests cannot be combined, as indeed they have been in the power-laundry field, to more quantitatively estimate the soil removal results obtained.

*Summary.* No soil or soiled fabric has been accepted as standard for two reasons: 1. No agreement concerning the type of soil has been reached. 2. Data are generally lacking to demonstrate that soiled fabrics reported, even though admittedly curtailed in scope, are standardized. That the process of controlled washing and of preparation of soiled fabric are difficult has been pretty well understood by those who have had any contact with the field.

It certainly is apparent that investigation in this field should not be undertaken with the idea that, like a short analytical procedure, it can be performed periodically with the expectation that reproducible data will be obtained. Although soiled test fabrics are now commercially available, this does not signify their standardization to a given degree of reproducibility nor correlation with practice.

The procedure for soiled fabric preparation and wash test method was detailed here to serve as an example of the effort required to produce a stand-

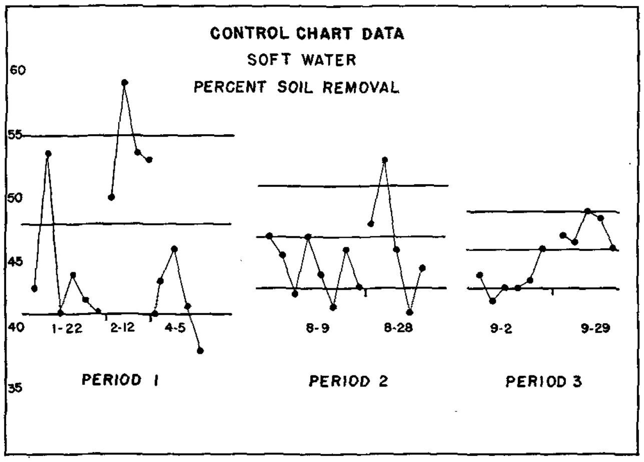

FIG. 6. Quality control chart.

ardized soil, and perhaps to act as a guide in advancement of this field as a whole.

It is granted that the reflectance method for evaluation is comparative rather than absolute, but reflectance *is* the measure generally used for estimation of cleanliness. Soiled test fabrics are currently used in screening operations and as a quick guide to research and development. Successful evaluation of detergents is accomplished by preliminary evaluation in a laboratory washer with standardized soiled fabric, followed and supplemented by practical laundering tests in the equipment and with the soiled articles it is expected the detergent will be required to clean.

There doubtless are other variants in procedure which have been operated as successfully as the one described. It should be heartening to realize that moderate success in standardization of a soil and wash test method has been achieved, and simultaneously discouraging to confirm the tremendous amount of effort required to attain such standards.

### Acknowledgment

Fully appreciated is the encouragement of management in permitting us free scope in our standardization and evaluation work and also the close cooperation of those many persons who have performed these tests.

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# Physical Properties of Fatty Acids. I. Some Dilatometric and Thermal Properties of Stearic Acid in Two Polymorphic Forms

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DILATOMETRY as a means of determining the expansibility of fatty acids has heretofore been employed by only one investigator (1). Moreover the dilatometers used in this early work were of the volumetric type, and the fatty acid samples evidently contained impurities since their reported melting points are not consistent with the values now accepted for these compounds when of the highest purity.

The ability of stearic acid to exist in different polymorphic modifications and data with reference to the long diffraction spacings of these modifications have been reported by a number of workers (2, 3, 4, 5). It has been stated (6) that the volume changes accompanying the transformation of stearic acid from one polymorphic form to another were unobservable and therefore the conditions with respect to the polymorphic transition of stearic acid have not been completely established.

Garner and co-workers (7) have reported some of the thermal properties of the *n*-aliphatic fatty acids, but detailed data for the specific heat, heat of fusion, and molal entropy of stearic acid are not available.

The purpose of the present investigation has been to determine certain useful physical properties of stearic acid, including a) its expansibility in the solid and liquid states, b) the temperature and volume changes associated with the polymorphic transformation of this acid, c) the absolute density and specific volume, d) the specific heat and heat of fusion, and e) the entropy calculated from heat capacity data.

### Preparation of Stearic Acid

A commercial product containing about 85% stearic acid was subjected to sulfonation followed by water washing to remove unsaturated impurities. The saturated fatty acid fraction was esterified with methanol and fractionally distilled, the methyl stearate converted to stearic acid, repeatedly recrystallized from acetone, and dried over phosphorous pentoxide. Characteristics of the purified stearic acid were: setting point, 69.20°C.; melting point, 69.5°C.; and absolute density, 0.8474 g./ml. at 72.0°C.(±0.05°).

### X-Ray Examination of the Samples

Slow crystallization of the purified stearic acid from benzene at room temperature and from hot glacial acetic acid yielded two distinct polymorphic forms. The crystals of stearic acid obtained from benzene were transparent, monoclinic, and variable in size, the largest being approximately 6 x 6 x 3 mm. A tendency toward crystal-twinning was noted. The X-ray diffraction pattern of these crystals exhibited a long spacing characteristic of the B-form while the crystals obtained from hot glacial acetic acid were opaque and flaky, and not characteristic with respect to size or system. These latter crystals exhibited a shorter diffraction spacing characteristic of the C-form of the acid. Although crystallization from benzene at room temperature yielded crystals corresponding to the B-form of the acid in every case, crystallization from this solvent above 53°C. resulted in the C-form. Likewise crystallization of stearic acid from glacial acetic acid at temperatures below 35°C. resulted in the B-form of stearic acid. These observations would indicate that the spacing exhibited by stearic acid is dependent upon the temperature at which crystallization occurs with either benzene or glacial acetic acid as the solvent. Crystallization at temperatures above the transition point results in the stable C-form of stearic acid and below

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