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DETERGENT COMPOSITION CONTAINING SOIL-REDEPOSITION INHIBITOR

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This invention relates to an improved method for promoting the soil-suspending power of detergents, in order to increase the whiteness retention of fabrics laundered therewith.

In copending application Serial No. 487,690, filed February 11, 1955, and now abandoned, assigned to the assignee of the present application, there is described a method for the use of hemicellulose as an additive for promoting the soil-suspending power of detergents. We have now discovered that certain derivatives of hemicellulose, as well as of other polysaccharides and natural gums, when employed in the manner herein described, result in even more notable improvements in the soil-suspending power of detergents.

The detergent or cleansing action of soaps and synthetic detergents is a complex process involving many factors. Essentially the process involves three stages: bringing the cleansing solution into intimate contact with the material to be cleaned (wetting); the removal of the soil from the fabric by a number of mechanisms (displacement, solubilization, neutralization, emulsification, peptization, ion-exchange, etc.); and the retention of the thus removed dirt in the detergent solution to prevent it from redepositing on the fabric. It is the last-named phase of the cleansing process with which our invention is concerned.

Atlhough the synthetic organic detergents are very effective in removing soil from fabrics, it is well-known that most synthetic detergents have a much poorer dirt-suspending power than the common water-soluble soaps (e.g., the soluble alkali-metal salts of long chain aliphatic carboxylic acids). While the present invention pertains more broadly to a method and means for promoting the soil-suspending power of detergents and soaps, it is a particular object of the invention to devise a method and means for improving the soil-suspending power of synthetic detergents.

When the dirt-suspending properties of a cleansing or washing solution are poor, the soil is redeposited on the fabric, before the latter is removed from the cleaning medium. This redeposition makes itself evident in a loss of whiteness of white goods, and of brightness in dyed goods. White fabrics, under such conditions, become grey. The property of soil suspension in washing solutions is thus often measured in terms of the "whiteness retention" of the fabric.

Since the ability of a detergent solution to prevent soil redeposition is just as important as its ability to remove the soil initially, it has been found necessary to improve the soil-suspending powers of most synthetic detergents. Attempts have been made to accomplish this by the use of additive materials referred to variously as whiteness-retention promoters, soil-suspending agents, anti-greying agents and anti-redeposition agents.

The previously mentioned copending application deals with the use of hemicellulose as an additive to detergents for the above-described purpose, it having been found that hemicellulose functions to impart substantial improvements in the whiteness retention of detergents.

We have now found that the polysaccharide derivatives obtained by the cyanoalkylation of starches, hemicellulose, cellulose and various natural gums, result in even more notable improvements when used as whiteness retention promoters. The cyanoalkyl derivatives of these

polysaccharides are most conveniently obtained by treatment with acrylonitrile, chloracetonitrile, chlorobutyronitrile or similar reagents which are capable of introducing cyanoalkyl groups. Means for the cyanoalkylation of polysaccharides are known to the art, ordinarily involving merely the mixing of the polysaccharide, suspended in an aqueous alkaline solution, with acrylonitrile or equivalent cyanoalkylating agent. As a result of the ensuing etherification reaction, a polysaccharide ether is produced which contains the cyanoalkyl groups.

It should be pointed out that in order to be of value for the purposes of our invention, the cyanoalkylated polysaccharide should be one which is dispersible in water at the pH conditions ordinarily prevailing in laundry operations. It is known that when polysaccharides contain too great a proportion of cyanoalkyl groups they tend to become indispersible in water. Therefore, in cyanoalkylating a polysaccharide, or in choosing a cyanoalkylated polysaccharide, for the purposes of this invention, it is important to ascertain that the degree of substitution has not reached the point where the product can no longer be dispersed in water to form a hydrated colloidal dispersion. It is understood, of course, that the polysaccharide need not necessarily be soluble in cold water, but must at least be capable of forming a dispersion in hot water.

As will be seen from some of the subsequent examples, the effectiveness of the cyanoalkylated polysaccharide as a whiteness retention promoter tends to vary with the degree of cyanoalkylation. Thus, a given polysaccharide with a higher percentage of cyanoalkyl groups may prove more effective than the same polysaccharide with a lower degree of cyanoalkylation. Yet it is sometimes found that as one passes a point of optimum effectiveness for a given base material, increasing the degree of cyanoalkylation still further (even though water dispersibility is still retained) sometimes tends to reduce the whiteness promotion effectiveness. Considering the great number of polysaccharide bases which are suitable for our invention, and the fact that the maximum desirable degree of cyanoalkylation is different for each polysaccharide base, it is seen that the preferred limits of cyanoalkylation cannot be stated in absolute figures. However, it is a matter of the simplest experimentation for the person in the art to determine for any given base the degree of cyanoalkylation which will give him the optimum degree of whiteness retention.

Among the polysaccharides which we have found to be most valuable for the production of cyanoalkylated derivatives, for use as whiteness retention promoters, are starches, water-dispersible cellulose ethers, hemicellulose and natural gums such as guar and locust beam gum. The starches may be from any source, including corn, waxy maize, tapioca, sago, potato, rice and wheat, and may be in their native state or may have been treated by chemicals and/or heat to produce so-called thin-boiling or fluidity starches, hydrolysis products, ethers or esters or other derivatives, so long as the starch product is still a water-dispersible polysaccharide.

Hemicellulose naturally occurs in plant materials in a water-insoluble form. In order to liberate the hemicellulose from the cell walls of the plant, the plant material may be treated with an aqueous alkali solution, at a pH of about 10 or higher. There is a pH-time-temperature relationship generally applicable in the extraction of the hemicellulose. Thus, at relatively low pH (say 10), elevated temperature is required for satisfactory hemicellulose extraction. As the temperature is increased, less time is required. With higher alkalinity, lower temperatures are usually sufficient for satisfactory hemicellulose extraction.

After the treatment to liberate the hemicellulose com-

ponent of the plant material, the entire extraction mixture containing the solubilized hemicellulose and the residual plant material may be adjusted with water to a suitable volume and slurry consistency to allow separation of the aqueous hemicellulose dispersion by filtration or centrifuging. The hemicellulose, which is thus obtained as an aqueous solution or colloidal dispersion, may then be isolated, with or without further pH adjustment, by drying over heated drums, spray drying or by other suitable drying means. Alternatively, the hemicellulose may be isolated by precipitation from the dispersion with organic solvents such as alcohol, acetone, etc., the precipitate being then separated and dried by any suitable means.

As the alkaline medium in extracting the hemicellulose from the plant material, one may employ the alkali-metal or alkaline earth hydroxides, ammonium hydroxide, alkali-metal carbonates or other suitable basic materials.

It will be obvious that we are not limited to any particular means of treating the plant material to solubilize the hemicellulose, the invention resting in the discovery that hemicellulose of such plant materials, solubilized by whatever means, and cyanoalkylated, is notably effective as a detergent whiteness-retention additive. Means for solubilizing the hemicellulose content of plant materials are known to those in the art. Thus, for example, one such method is described in an article by Wolf et al. in "Cereal Chemistry," vol. 30, pages 451–70, 1953, entitled "Preparation and Properties of Hemicellulose From Corn Hulls."

Instead of cyanoalkylating hemicellulose in the relatively pure state, obtained as indicated above by alkali separation from hemicellulose-containing plant materials, we have also found it possible to cyanoalkylate the crude material resulting from the alkali treatment of the plant portion, without actual physical separation of the hemicellulose component. In other words, after treating the plant material with aqueous alkali at a given temperature and for a given time, as indicated above, or in conjunction with such alkali treatment the cyanoalkylating agent (e.g. acrylonitrile) is added, and the entire mass is thereafter dried by any suitable means and used as a whiteness retention additive. In such material, which we shall hereafter refer to as "cyanoalkylated crude hemicellulose," the hemicellulose has been liberated from the plant walls, rendered water-dispersible and cyanoalkylated, but is present together with the other plant portions. Because only a portion of the crude hemicellulose is hemicellulose proper, it is ordinarily necessary, in order to obtain a given degree of whiteness retention, to employ more of the crude material than when using the relatively pure, separated, cyanoalkylated hemicellulose.

The cyanoalkylated polysaccharide derivative may be blended in dry form with the detergent, or a solution or slurry of the derivative may be mixed with the detergent or detergent formulation and the entire mixture dried by any suitable means. Alternatively, the cyanoalkylated polysaccharide may be added to the actual washing solution containing the detergent.

As is known, synthetic detergents fall into three main classifications, depending upon their electrolytic character—cationic, anionic and nonionic. These are all surface-active agents and have structurally unsymmetrical molecules containing both hydrophilic, or water-soluble, groups and oil-soluble hydrocarbon chains. The cationic detergents are positively charged, the anionic are negatively charged and the nonionic detergents are neutral. Our invention is effective with all three types, but is of particular value with regard to the latter two types. Representative examples of cationic detergents are the high molecular weight imidazolinium chloride (mol. wt. 370) sold under the trade name "Quaternary C" by the Alrose Chemical Company, and the monostearyl ethylene diamine trimethyl ammonium methyl sulfate sold under the trade name "Sapamine K.W.C." by the Ciba Company Inc. Representative examples of some anionic detergents are sodium lauryl sulfate, sulfated monoglyceride (as for example that made from coconut oil and sold by the Colgate-Palmolive Co. under the trade name "Monad G"), and sulfonate types such as the N-octadecyl tetrasodium (1,2-dicarboxylethyl sulfosuccinamate) sold under the trade name "Aerosol 22" by the American Cyanamid Company, and the sodium dodecyl benzene sulfonate sold under the trade name "Santomerse 80" by Monsanto Chemical Co. Representative examples of nonionic synthetic detergents include the aromatic polyglycol ether condensate sold by the Onyx Oil & Chemical Co. under the trade name "Neutronyx 600," as well as the polyoxyethylene ester sold by Monsante Chemical Company under the trade name "Sterox CD." It is understood, of course, that these detergents are listed merely by way of illustration and not as any limitation upon the scope of the invention.

The proportion of the cyanoalkylated polysaccharide derivative to be added to the detergent, in order to obtain optimum results, will vary, depending upon the particular derivative, the degree of cyanoalkylation and the detergent used. In general, we have found that substantial improvements in whiteness retention were obtained when using anywhere from 0.05% of the polysaccharide additive, based on the weight of the detergent, to as much as 250%. Since the detergent proper is ordinarily only about one-fifth of the built detergent, as will be seen from the representative formulation in Example VII, this amounts to a range of from 0.01% to 50% based on the built detergent. Where a built detergent is employed which contains a different proportion of active detergent, these figures can of course be easily adjusted. Simple experimentation will indicate the optimum quantity for any particular combination of detergent and additive. In general we prefer to use quantities of the polysaccharide additive within the range 0.05% to 25.0% based on the detergent.

When using cyanoalkylated starches, we have found it preferable to use thinner boiling types of starches, such as those that have been lightly converted with acids or oxidizing agents to the degree known in the trade as 60 to 90 fluidity.

We have also found that when the cyanoalkylated polysaccharides, and particularly cyanoethyl starch, are used in admixture with carboxymethylcellulose as additives to detergents, the resulting improvement in whiteness retention is often greater than that which is observed from the use of either the starch derivative or the carboxymethylcellulose alone. The relative proportions of cyanoalkylated starch and carboxymethylcellulose for optimum effectiveness will vary with the degree of cyanoalkylation and the level of addition (percent on the detergent) as well as with the particular detergent formulation employed. This synergistic effect of the combination of cyanoalkylated polysaccharide and carboxymethylcellulose was surprising and unpredicted and constitutes an important aspect of our invention.

In the following examples we illustrate the cyanoalkylation of various polysaccharides, it being remembered, however, that our invention is not limited to any one particular method of cyanoalkylation.

Example I

21.5 grams (dry basis) of hemicellulose derived from corn bran were dispersed in a solution of 3.5 grams sodium hydroxide in 200 ml. water. 4.9 grams of acrylonitrile were aded dropwise, over a period of 15 minutes at room temperature (25–30° C.). After agitating for four hours at room temperature, the reaction mixture was adjusted to pH 4.5 with dilute hydrochloric or glacial acetic acid and poured with vigorous agitation into 2 volumes of ethyl alcohol. The precipitated product was washed by decantation with more alcohol, filtered, washed on the filter with alcohol and ether, then air dried. The 20.4 grams (dry basis) of product thus obtained contained

11% cyanoethyl groups, as calculated from Kjeldahl nitrogen analysis.

The above procedure was repeated, using 22.3 grams of hemicellulose, 4 grams of sodium hydroxide, 13.3 grams of acrylonitrile and 400 ml. water. The resulting product was found to contain 16.7% cyanoethyl groups.

When the same procedure was again repeated, but using 22.3 grams hemicellulose, 4.9 grams sodium hydroxide, 8.8 grams acrylonitrile and 400 ml. water, the resulting product was found to contain 6.2% cyanoethyl groups.

Example II

22.4 grams (dry basis) of hemicellulose derived from corn cobs were dispersed in a solution containing 6.4 grams sodium hydroxide in 400 ml. water. 8.5 grams acrylonitrile was added dropwise to the stirred reaction mixture. After four hours at room temperature, the mixture was neutralized, and the cyanoalkylated hemicellulose was separated and washed as described in Example I. It was found that the 18.5 grams of product thus obtained contained 10.9% cyanoethyl groups.

Using the same proportions and procedures as above, rock maple hemicellulose was cyanoethylated to contain 4.4% cyanoethyl groups; birch hemicellulose to 10.8% cyanoethyl groups; oat hemicellulose to 14.0% cyanoethyl groups.

Example III

29.6 grams of locust bean gum (ash-free, dry basis) were dispersed in a solution of 7.4 grams sodium hydroxide in 300 cc. of a 45% aqueous solution of sodium sulfate. 9.9 grams of acrylonitrile was added dropwise at room temperature, as previously described. After three hours, the product precipitated. Stirring was continued for an additional hour, the reaction mixture was acidified, and the precipitated product separated by centrifuging. After washing with alcohol and ether, the product was air-dried to yield 33.5 grams of a cyanoethylated gum containing 18.1% cyanoethyl groups.

Example IV

This example illustrates the cyanoethylation of crude corn bran hemicellulose, wherein the hemicellulose has not been separated from the plant portions. 50 grams of coarse bran from the corn wet-milling process were dispersed in a solution of 3.5 grams sodium hydroxide in 500 ml. water, and heated with agitation at 95–98° C. for 1 hour to liberate and solubilize the hemicellulose. The reaction mixture was cooled to room temperature, and there were added an additional 3.5 grams sodium hydroxide and 9.6 grams acrylonitrile, the reaction continuing at room temperature over a period of 4 hours. The reaction mixture was acidified, precipitated in alcohol (to remove the salts formed by the neutralization), and the precipitate collected by filtration, washed with alcohol and ether and air-dried. The material thus obtained was found to contain 9.8% cyanoethyl groups.

Example V

This example illustrates the cyanoethylation of methyl cellulose (a water-dispersible derivative of cellulose). 70.2 grams, dry basis, of methyl cellulose (of the type sold by The Dow Chemical Company under the trade name "Methocel" 15 cps.) were dispersed in 400 ml. water at 80° C., with agitation. The solution was cooled and there were added 800 ml. water containing dissolved therein 16.8 grams sodium hydroxide. 36.3 grams of acrylonitrile were then added dropwise over a period of 15 minutes. The solution was agitated at room temperature and samples were removed after 50 minutes, 2 hours, and 4 hours. The various samples were acidified with glacial acetic acid to pH 4.5 and precipitated with acetone and dried in an oven. It was found that the samples contained 7.1%, 7.9% and 16.3% cyanoethyl groups respectively, as calculated from Kjeldahl nitrogen analysis.

Example VI

This example illustrates the cyanoethylation of an oxidized corn starch. 200 pounds of corn starch which had been chlorinated to a degree known in the trade as 78–79 fluidity were suspended in 400 pounds of water. With continuous agitation of the slurry there were slowly added 10 pounds of acrylonitrile followed by the slow addition of 64 pounds of a 25% aqueous sodium hydroxide solution. Agitation was continued at room temperature 8 to 16 hours, whereupon the reaction mass was neutralized with acid to pH 6 and precipitated in a large excess of ethanol. The precipitate was filtered, washed with ethanol and dried in vacuo. In alternate examples the above procedure was repeated except that instead of obtaining the product by alcoholic precipitation, the reaction mass, after neutralization, was in one case spray dried, and in another case, passed over heated rolls to give a drum dried starch derivative.

Example VII

Example VI was repeated, in several modifications as follows:

(*a*) Same as Example VI, but using 60 pounds of acrylonitrile.

(*b*) Same as Example VI, but using 100 pounds of acrylonitrile.

(*c*) Same as Example VI, but reducing the water from 400 pounds to 200 pounds, increasing the amount of acrylonitrile from 10 pounds to 40 pounds, using 60 pounds of a 50% sodium hydroxide solution instead of 64 pounds of a 25% sodium hydroxide solution, and cutting the reaction time to 6 hours.

(*d*) Same as Example VI, but using a 2-hour reaction period.

(*e*) Same as (*c*), but reducing the quantity of 50% sodium hydroxide solution from 60 pounds to 32 pounds.

(*f*) Same as (*a*), but using a corn starch which had been acid-converted to a degree known in the trade as 60 fluidity.

(*g*) Same as (*a*), but using a white corn dextrin having 85%–95% solubility in cold water.

(*h*) Same as Example VI, but using a chlorinated tapioca starch instead of chlorinated corn starch.

(*i*) Same as (*f*), but using a sago starch which had been acid-converted to a degree known in the trade as 60 fluidity.

All of these modifications, as well as the product of Example VI were cyanoethylated polysaccharide derivatives which proved to be notably effective as additives to detergents for promoting whiteness retention.

In the following examples we shall illustrate the use of cyanoalkylated polysaccharides as whiteness retention detergent additives. However, it is first necessary to describe the method that was used to evaluate the effectiveness of these polysaccharide derivatives in increasing whiteness retention.

The effectiveness of cyanoalkylated polysaccharide derivatives in promoting whiteness retention (i.e., in preventing soil redeposition) was evaluated by a procedure adapted from that described in an article by Vaughn and Smith, Journal of the American Oil Chemists Society, 25, 44–51 (1948). Essentially, the evaluation is based upon the photometric measurement of carbon deposition on unsoiled cotton fabric subjected to a detergent solution that includes a standard quantity of carbon black and the desired quantity of the additive to be tested. The details of the procedure are as follows:

(*a*) Clean, unsized, bleached cotton muslin was cut into 2½" x 3½" swatches.

(*b*) A standard soil solution was prepared by diluting 28.55 grams of a carbon black paste (as sold by Binney & Smith Co. under the trade name "Aquablak B," and having 35% solids content and an average particle size of 28 mu) with distilled water to one liter. This yielded a 1% stock solution.

(*c*) A detergent solution was prepared by dissolving 2.5 grams "Santomerse 80," 1.5 grams anhydrous sodium sulfate (C.P.), 1.0 gram sodium metasilicate (Tech.) and 5.0 grams of sodium tripolyphosphate in 190 ml. of water. This yields a solution containing 1% active detergent, or 5% "built" detergent. It is customary, in the laundering trade, to add various salts and alkaline materials to detergents, to enhance the detergent efficiency. Such mixtures are known as "built" detergents, and in the above-described compound, the salts comprise the builder.

(*d*) The cyanoethylated polysaccharide additive solution was prepared by dissolving 0.5 gram of the particular polysaccharide derivative to be tested, in 200 ml. water. This solution contains approximately 0.25% solids.

(*e*) The actual test solution was then prepared by mixing 5 ml. of the detergent solution (*c*), 3 ml. of the additive solution (*d*), and 5 ml. of the standard soil solution (*b*), with 93 ml. of water in a pint jar. 15 steel balls (¼" diameter) were added and the contents of the jar mixed well. This mixture is in effect a 0.24% solution of built detergent with 3% cyanoethylated polysaccharide additive based on the weight of the built detergent. The concentration of additive in the test washing solution is approximately 0.007%, and the concentration of carbon black 0.047%.

(*f*) A number of pint jars were filled with the test solution as described in (*e*), and two cotton swatches were added to each jar. The lids of the jars were closed tightly, and the jars rotated, end over end, in a constant temperature bath set at 140° F. for 20 minutes.

(*g*) The swatches were then removed, rinsed separately by dipping and swirling three times in each of three 2-liter beakers of distilled water, gently blotted on absorbent paper to remove excess water, and then ironed dry.

(*h*) The degree of whiteness retention was then determined by measuring the light reflectance of the dry swatches on a Hunter Multipurpose Reflectometer, standardized to a reflectance of MgO=100%. The original cloth before immersion in the test solution had a reflectance rating of 86.7% (based on MgO=100%). The degree of whiteness retention was calculated by the following equation:

$$W=\frac{R}{R_1}\times 100$$

where W is the percent whiteness retention, R is the reflectance value of the test swatch, and R_1 is the reflectance value of the original cloth swatch before immersing in the test solution (i.e. 86.7). The increase in whiteness retention due to the cyanoethylated polysaccharide additive was calculated according to the following equation:

$$W_1=W-W_0$$

where W_0 is the percent whiteness retention of a swatch treated with detergent solution containing no additive (control), W is the percent whiteness retention given by a swatch treated with detergent containing the additive, and W_1 is the increase in whiteness retention of the detergent containing the additive as against the control. The percent increase in whiteness retention due to cyanoalkylation is obtained by calculating the difference between the percent whiteness retention when using the cyanoalkylated additive and when using the non-cyanoalkylated polysaccharide, dividing this figure by the percent whiteness retention using the non-cyanoalkylated polysaccharide, and multiplying the resulting figure by 100.

As will be noted from paragrah (*c*) above, the built detergent comprised one part actual active detergent to 4 parts of builder materials. ("Santomerse 80" contains 80% active detergent.) Thus, the active detergent comprised one-fifth of the total built detergent. Therefore, in evaluating the figures where this detergent formulation is used, it is simple to convert the percentage of polysaccharide based on the built detergent into a percentage based on the actual active detergent, merely by multiplying the former figure by five.

Example VIII

In this example we list the values obtained when swatches of fabric were tested, according to the procedure described above, with detergent containing various cyanoethylated polysaccharides. In all of these, the detergent was "Santomerse 80," and 3% of the cyanoalkylated polysaccharide derivative was present, based on the weight of the built detergent. The value for the control W_0 in this series (that is, the percent whiteness retention given by the detergent without the hemicellulose additive) was 10.6

Additive	Percent cyanoethyl groups	W	W_1	Percent increase in whiteness retention due to cyanoethylation
Corn bran hemicellulose	0	39.7	29.1	
Cyanoethyl corn bran hemicellulose	2.2	42.0	31.4	6
Do	13.0	61.6	51.0	55
Do	18.4	50.4	39.8	27
Corn cob hemicellulose	0	35.1	24.5	
Cyanoethyl corn cob hemicellulose	10.9	57.3	46.7	63
Rock maple hemicellulose	0	18.2	7.6	
Cyanoethyl rock maple hemicellulose	10.5	62.9	52.3	25
Alkali treated corn bran	0	33.4	22.8	
Cyanoethyl alkali treated corn bran	10.5	53.3	42.7	60
Guar gum	0	25.7	15.1	
Cyanoethyl guar gum	3.2	43.3	32.7	69
Dextran	0	18.0	7.4	
Cyanoethyl dextran	9.7	42.2	31.6	135
78 fluidity chlorinated corn starch	0	18.3	7.7	
Cyanoethyl 78 fluidity chlorinated corn starch	15.2	47.5	36.9	160
Do	21.2	51.8	41.2	183
Do	34.2	45.4	34.8	148
85 fluidity chlorinated tapioca starch	0	16.4	5.8	
Cyanoethyl 85 fluidity chlorinated tapioca starch	2.2	18.5	7.9	13
73 fluidity acid-converted sago starch	0	18.9	8.3	
Cyanoethyl 73 fluidity acid-converted sago starch	20.1	51.5	40.9	172

It is seen from the above table that the use of the cyanoalkylated polysaccharide in every case resulted in an increase in whiteness retention, as compared to the corresponding non-cyanoalkylated polysaccharide. Thus, an untreated corn bran hemicellulose gave a figure of 39.7% whiteness retention. Since the control (the test swatch treated with detergent containing no polysaccharide additive) showed a whiteness retention of only 10.6, this means that the untreated hemicellulose resulted in an increase of 39.7 minus 10.6, or 29.1 in whiteness retention. On the other hand, a cyanoethylated corn bran hemicellulose containing 2.2% cyanoethyl groups gave 42.0% whiteness retention; a corn brand hemicellulose containing 13% cyanoethyl groups showed a whiteness retention of 61.6%. The latter figure represents a percentage increase of 55% in whiteness retention over that of the non-cyanoalkylated hemicellulose. Similar remarkable improvements in whiteness retention are noted in the case of the other cyanoalkylated polysaccharides.

Example IX

In this example we present further values obtained by testing swatches of fabric, according to the previously described procedure, with detergent containing various cyanoalkylated polysaccharides. The detergent was the same as that used in Example VIII. The value for the control W_0 in this series (that is, the percent whiteness

retention given by the detergent without the hemicellulose additive) was 7.6.

Additive	Percent cyanoethyl groups	W	W_1	Percent increase in whiteness retention due to cyanoethylation
Methyl cellulose	0	28.7	21.1	
Cyanoethyl methyl cellulose	7.9	49.3	41.7	72
Do	16.3	59.8	52.2	108
Hydroxyethyl cellulose	0	12.8	5.2	
Cyanoethyl hydroxyethyl cellulose	7.3	19.1	11.5	49
Do	11.1	24.9	17.3	97
Larchwood arabogalactan	0	12.2	4.6	
Cyanoethyl larchwood arabogalactan	17.1	39.8	32.2	226
78 fluidity chlorinated corn starch	0	19.4	11.8	
Cyanoethyl 78 fluidity chlorinated corn starch	22.2	68.9	61.3	255

From the above figures it is seen that the effectiveness of cyanoalkylation is notable with a wide variety of polysaccharides. Thus, whereas untreated methyl cellulose indicated a whiteness retention of 28.7%, the same methyl cellulose cyanoethylated to contain 7.9% cyanoethyl groups gave a whiteness retention figure of 49.3%, and when the degree of cyanoethylation was increased the whiteness retention rose to 59.8%. Thus the methyl cellulose containing 16.3% cyanoethyl groups showed an increase in whiteness retention of 108%, as compared to the untreated methyl cellulose. Similarly improved effectiveness is shown for the various other types of polysaccharides.

Example X

This example illustrates the effect of varying amounts of the cyanoalkylated polysaccharide additive, when used with the built "Santomerse 80" detergent of Examples VIII and IX. In this example, additive "A" was a cyanoethylated corn bran hemicellulose, containing 13% cyanoethyl groups. Additive "B" was a cyanoethylated 78 fluidity chlorinated corn starch, containing 22.2% cyanoethyl groups. In the case of "A," the control W_0 was 10.6. In the case of "B," W_0 was 7.6.

Additive	Percent additive on built detergent	W (percent whiteness retention)
A	1	56.4
A	3	61.6
A	5	64.0
A	10	69.4
A	20	65.6
A	50	60.7
B	0.05	30.1
B	0.1	39.4
B	0.2	57.4
B	0.4	50.9
B	0.8	63.4
B	1.0	76.0
B	2	81.4
B	10	85.6
B	15	84.5
B	25	83.1
B	35	85.4
B	50	84.3

It is seen from the above that although varying amounts of the cyanoethylated additive do result in differences in the degree of whiteness retention, notable improvements are achieved throughout the wide range of proportions.

Example XI

This example illustrates the evaluation of test swatches washed with various detergents and cyanoalkylated polysaccharides. In all cases 3% of the polysaccharide additive was used, based upon the detergent (built or unbuilt, as specified). The control W_0 (percent whiteness retention when using detergent without additive) was 9.6 in the case of "Duponol ME" plus builders; 44.3 in the case of "Duponol ME" without builder; 58.5 in the case of "Monad G"; 62.1 in the case of Ivory soap; 44.5 in the case of "Neutronyx 600"; 70.8 in the case of "Stearox CD."

Sample description	Percent cyanoalkylation groups	Detergent	W	W_1	Percent increase in whiteness retention due to cyanoalkylation
Corn bran hemicellulose	0	Duponol ME plus builder	39.6	30.0	
Cyanoethyl corn bran hemicellulose	13		53.3	43.7	35
Corn bran hemicellulose	0	Duponol ME (no builder)	81.5	37.3	
Cyanoethyl corn bran hemicellulose	13		86.1	41.8	6
78 fluidity chlorinated corn starch	0	Monad G	66.9	8.4	
Cyanoethyl 78 fluidity chlorinated corn starch	22.2		69.3	10.8	4
Corn bran hemicellulose	0	Ivory soap	78.0	15.9	
Cyanoethyl corn bran hemicellulose	13		80.4	18.3	3
78 fluidity chlorinated corn starch	0	Neutronyx 600	48.2	3.7	
Cyanoethyl 78 fluidity chlorinated corn starch	22.2		51.7	7.2	7
78 fluidity chlorinated corn starch	0	Stearox CD	51.5	−19.3	
Cyanoethyl 78 fluidity chlorinated corn starch	22.2		73.1	2.3	42

NOTE.—"Duponol ME" is sodium lauryl sulfate, technical.

Although a variety of detergent types are shown above, it is seen that the addition of a cyanoalkylated polysaccharide causes all of them to give improved whiteness retention.

Example XII

This example illustrates the evaluation of test swatches, according to the method already described, but using a lower concentration of soil. The detergent employed was "Monad G," with builders, so that the active detergent comprised 31% of the total detergent, with about 8.7% sodium pyrophosphate and about 60% sodium sulfate. The test solution was so proportioned that it contained 0.047% active detergent and only 0.028% "Aquablak B" carbon black, as against 0.047% carbon black in the previous tests. The polysaccharide additive in this case was a corn starch which had been oxidized by chlorination to the degree known in the trade as 85 fluidity, and cyanoethylated to contain 20% cyanoethyl groups. In the following table, the percent whiteness retention is shown for various percentages of the cyanoethylated additive, based on the active detergent. Since the active detergent comprised roughly one-third of the total built detergent, the figures below for "Percent Additive on Active Detergent" may easily be converted to "Percent Additive on Built Detergent" by dividing the former by three. Thus, 0.03% additive on active detergent is equivalent to 0.01% on the built detergent.

Percent additive on active detergent	Percent whiteness retention
Control [1]	40.0
0.03	47.8
0.09	58.5
0.15	63.7
3.0	45.4
9.0	61.3

[1] Detergent without polysaccharide additive.

It is seen that very substantial improvements are obtained by the use of the cyanoalkylated additive.

Example XIII

This example illustrates the effect of mixtures of a cyanoalkylated polysaccharide and carboxymethylcellulose. The carboxymethylcellulose was that sold by The Hercules Powder Co. under the trade name "CMC 70 LL" (0.6–0.85 carboxymethyl groups per anhydroglucose unit, 100% active), and the polysaccharide was a cyanoethylated 78 fluidity chlorinated corn starch (33.5% cyanoethyl groups). The additive (starch or CMC or mixture of both) was used in the amount of 0.5%, based on the weight of the built "Santomerse 80" detergent. Whiteness retention was calculated from reflectance readings made with the Photovolt Corporation Photoelectric Reflection Meter, Model 610, standardized to MgO=100%, using Tristimulus green filter.

Additive ratio, starch to CMC	W (percent whiteness retention)
100:0	60.1
0:100	48.0
95:5	67.9
80:20	71.5
50:50	62.0

The above example was repeated except that in place of the cyanoethylated chlorinated corn starch, we employed a cyanoethylated corn bran hemicellulose, containing 13% cyanoethyl groups. The additive (hemicellulose or CMC or mixture of both) was used in the amount of 3.0% based on the weight of the built detergent. The following are the whiteness retention figures obtained when using various combinations of the carboxymethylcellulose and cyanoethylated hemicellulose.

Additive, hemicellulose to CMC	W (percent whiteness retention)
100:0	35.6
0:100	57.8
80:20	62.4
50:50	73.7

It is seen from the above that mixtures of the cyanoalkylated polysaccharide and carboxymethylcellulose are indicated to be considerably more effective than either additive used alone.

It will be seen that the use of cyanoalkylated polysaccharides as additives to detergents results in remarkable improvements in whiteness retention. As explained, the cyanoalkylated polysaccharide should be in a form which is dispersible in water at the pH conditions normally prevalent in laundering operations, namely, approximately 8–12. A further aspect of our invention lies in the discovery of the particular synergistic effect of mixtures of

cyanoalkylated polysaccharides with carboxymethylcellulose, when used as additives to detergents, the mixture being found to be more effective as a whiteness retention promoter than either of the two components used alone.

It will be apparent that many variations in materials, proportions and procedures are possible, without departing from the scope and spirit of this invention.

We claim:

1. A synthetic organic detergent having incorporated therewith an agent for promoting the soil-suspending power of the detergent, said agent comprising a water-dispersible cyanoalkylated polysaccharide in an amount from 0.05% to 250% based on the weight of the detergent.

2. The detergent composition of claim 1 in which the detergent is a synthetic detergent having an anionic electrolytic character.

3. The detergent composition of claim 1 in which the detergent is a synthetic detergent having a nonionic electrolytic character.

4. A synthetic organic detergent having incorporated therewith an agent for promoting the soil-suspending power of the detergent, said agent comprising a water-dispersible cyanoalkylated polysaccharide obtained by the cyanoalkylation of polysaccharides selected from the group consisting of starches, cellulose, hemicellulose and natural gums in an amount from 0.05% to 250% based on the weight of the detergent.

5. A built synthetic organic detergent composition having incorporated therewith an agent for promoting the soil-suspending power of the detergent, said agent comprising a water-dispersible cyanoalkylated polysaccharide in an amount from 0.01% to 50% based on the weight of the built detergent.

6. A detergent composition consisting essentially of a water-soluble organic detergent selected from the group consisting of fatty acid soaps and synthetic organic non-soap detergents and, as a soil redeposition inhibitor, from about 0.1% to about 20% by weight of a cyanoethylated starch containing from about 2% to about 30% of cyanoethyl groups.

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