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**USE OF POLYVINYLPIRROLIDONE AS A SOIL-SUSPENDING AGENT**

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A non-exclusive, irrevocable, royalty-free license in the invention herein described, for all governmental purposes, throughout the world, with the power to grant sub-licenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to washing procedures particularly to the washing of textile materials such as fabrics and fibers with aqueous media. In particular the invention concerns the use of polyvinylpyrrolidone in the aqueous washing medium whereby to minimize the re-deposition of soil during the washing procedure.

It is well known in the art that a successful washing operation involves two separate factors, i.e., (a) the removal of dirt from the textile material and (b) keeping the soil suspended in the medium so that it will not be re-deposited on the textile. In general aqueous washing media containing soap fulfill both of these criteria as soap not only is a good soil remover but also keeps the removed soil in suspension so that little re-deposition takes place. However, the present trend is toward the use of anionic synthetic detergents such as the alkyl benzene sulphonates since these agents can be used in hard water areas as their detersive power is not decreased by the presence of calcium and magnesium ions. However, these anionic detergents have the disadvantage that their suspending power is poor. Whereas they are very effective from the standpoint of removing soil they are not so effective in preventing re-deposition and so cotton fabrics washed with such agents will be grayer than when using soap. In order to overcome this disadvantage, various soil suspending agents are commonly added to the anionic detergents. One of the most commonly used agents is sodium carboxymethyl cellulose.

It has now been found that polyvinylpyrrolidone has useful soil-suspending properties and when added to aqueous washing media the degree of soil re-deposition is greatly reduced. As well known in the art, polyvinylpyrrolidone is not a single, individual compound but may be obtained in almost any degree of polymerization. The degree of polymerization is most easily expressed in terms of average molecular weight. Although this invention comprises in its broad aspect the use of polyvinylpyrrolidone having any degree of polymerization and which is soluble in water at least to the extent of about .001% to about 0.1%, it is to be understood that not all the polymers possess the same degree of effectiveness. Thus as shown in the examples infra, polyvinylpyrrolidones having an average molecular weight from about 15,000 to about 40,000 exhibit maximum soil-suspending activity. For this reason it is preferred to use a polyvinylpyrrolidone of such molecular weight range as a soil-suspending agent in washing operations.

A particular advantage of polyvinylpyrrolidone as a soil-suspending agent is that it retains its effectiveness even in the presence of relatively high concentrations of calcium such as would be present in hard water. As

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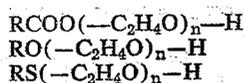
shown in Example II herein, this ability to retain effectiveness in hard water is not obtained in the case of the known soil-suspending agent, sodium carboxymethyl cellulose.

In applying this invention in practice the polyvinylpyrrolidone may be dispersed into the aqueous washing medium in a concentration from about 0.001 to about 0.1%—the higher proportions giving the greater degree of protection against soil re-deposition. It is obvious that the proportion of polyvinylpyrrolidone can be higher than the above range but in general increasing the concentration above 0.1% gives little if any added protection. If desired, the polyvinylpyrrolidone can be incorporated with the detergent so as to form a composition which on dissolving in water furnishes the desired washing medium. To this end, the detergent is mixed with about 2 to 10% of the polyvinylpyrrolidone.

In carrying out washing operations in accordance with this invention, the fabric or other textile material is agitated in the usual manner preferably at elevated temperatures as commonly used in laundries with the aqueous media containing the polyvinylpyrrolidone and the detergent. As the detergent one may use any of the materials commonly used for washing purposes.

The detergent may be, for example, of the anionic or non-ionic types. In the first category are included ordinary soaps, that is, sodium or potassium salts of the higher fatty acids, or, usually, mixtures of higher fatty acids as are derived from naturally-occurring oils and fats. Also included in the anionic category are the detergents of the sulphonate or sulphate type. As well known in the art, a multitude of such materials are available, including the alkyl (C<sub>8</sub>-C<sub>18</sub>) sulphates, the alkyl (C<sub>8</sub>-C<sub>18</sub>) sulphonates, the alkyl (C<sub>8</sub>-C<sub>18</sub>) aromatic sulphonates, the mono- or di-alkyl (C<sub>6</sub>-C<sub>18</sub>) esters of sulphosuccinic acid, sulphonated or sulphated amides of the higher fatty acids such as N-sulphoethyl stearamide, and so forth. These compounds are generally employed in the form of their salts, i.e., their sodium, potassium, ammonium or amine salts. Some of the particular detergents which may be used are: sodium octyl sulphate, sodium nonyl sulphate, sodium decyl sulphate, sodium undecyl sulphate, sodium dodecyl sulphate, sodium tridecyl sulphate, sodium tetradecyl sulphate, sodium pentadecyl sulphate, sodium hexadecyl sulphate, sodium heptadecyl sulphate, sodium octadecyl sulphate, sodium oleyl sulphate, sodium octyl sulphonate, sodium nonyl sulphonate, sodium decyl sulphonate, sodium undecyl sulphonate, sodium dodecyl sulphonate, sodium tridecyl sulphonate, sodium tetradecyl sulphonate, sodium pentadecyl sulphonate, sodium hexadecyl sulphonate, sodium octadecyl sulphonate, sodium oleyl sulphonate, sodium salt of di-octyl sulpho-succinate, sodium octyl benzene sulphonate, sodium nonyl benzene sulphonate, sodium decyl benzene sulphonate, sodium undecyl benzene sulphonate, sodium dodecyl benzene sulphonate, sodium tridecyl benzene sulphonate, sodium tetradecyl benzene sulphonate, sodium pentadecyl benzene sulphonate, sodium hexadecyl benzene sulphonate, sodium heptadecyl benzene sulphonate, sodium octadecyl benzene sulphonate, sodium tri (isopropyl) benzene sulphonate, sodium tri (isobutyl) benzene sulphonate, sodium tri (isopropyl) naphthalene sulphonate, sodium tri (isobutyl) naphthalene sulphonate, and so forth. The commercially available detergents are generally not pure compounds but are mixtures of homologous compounds and are quite sat-

isfactory. Thus for example, the sodium alkyl benzene sulphonate wherein the alkyl group contains 12 to 18 carbon atoms is a well known detergent. Others are: a mixture of sodium alkyl sulphates consisting mostly of sodium lauryl sulphate; a mixture of sodium alkyl phenol sulphonates wherein the alkyl group contains 12 to 18 carbon atoms; and a mixture of sodium alkyl sulphonates wherein the alkyl group contains 10 to 18 carbon atoms. As non-anionic detergents one may employ polyalkylene glycol esters, ethers and thioethers of the following types:



wherein the R's represent long chain alkyl radicals of 8 to 12 carbon atoms and  $n$  is an integer from about 4 to 12. Other non-anionic detergents are the long-chain fatty acid esters of anhydrosorbitol, or the polyethylene glycol addition products of such esters. It is evident that the particular detergent used is not critical except that one should be chosen which is generally useful in emulsifying and detergent applications.

The concentration of the detergent is not critical within a wide range and depending on the soil removal efficiency of the particular agent, the range of concentration may be from about 0.05% to about 0.5%. If desired, the soil removal efficiency of the detergent may be increased by addition to the aqueous medium of any of the usual types of builders such as sodium hexametaphosphate, tetra-sodium pyrophosphate, sodium tripolyphosphate, tri-sodium phosphate, borax, sodium carbonate, sodium silicate, sodium metasilicate, and so forth.

The following examples illustrate the invention in greater detail. The known soil-suspending agent, sodium carboxymethyl cellulose, was employed in some of the experiments for comparative purposes. In all the experiments, carbon black was added to the washing media to test the soil-suspending power of the various materials under test. Obviously in practice of the invention, no carbon black or other soil would be added to the washing medium.

#### Example I

A series of experiments were carried out in which clean swatches of cloth were agitated in an aqueous medium containing a synthetic detergent, various soil-suspending agents at various concentration levels, and carbon black. The treated swatches were then subjected to reflectance measurements to measure the amount of soil (carbon black) which had been deposited on the fabric thus to compare the effectiveness of the soil-suspending agents. The reflectance values are an index of the cleanness of the cloth; the higher the proportion of light reflected the cleaner the cloth. In the examples the abbreviations "PVP" and "AMW" stand for polyvinylpyrrolidone and average molecular weight, respectively. The experiments were carried out as follows:

A standard washing medium was prepared containing: water; sodium alkyl ( $\text{C}_{12}-\text{C}_{18}$ ) benzene sulphonate, 0.12%; sodium tripolyphosphate, 0.08%; sodium carbonate, 0.04%; and carbon black, 0.1%. The pH of this solution was about 10.3. To samples of the standard medium were added various soil-suspending agents as hereinafter indicated. Each solution so prepared was tested as follows:

Two hundred cc. of the test solution was placed in a pint jar together with a swatch of a standard bleached muslin (cotton) cloth and 20 $\frac{1}{4}$ " stainless-steel balls. The jar was then sealed and placed in a "Lauderometer" and agitated by rotation at 140° F. for 20 minutes. The test swatch was then removed, rinsed 4 times with distilled water and agitated with 200 cc. of distilled water in the "Lauderometer" for 10 minutes at 140° F. This washing in distilled water was done to remove loosely

adherent carbon black so that the results would relate solely to adsorbed soil. The treated swatch was then dried in air, ironed, and the reflectance measured.

The materials, and proportions used and the results obtained are tabulated below:

Concentration of soil-suspending agent, percent	Reflectance (in percent) of washed samples using various soil-suspending agents at various concentration levels					
	PVP, A.M.W. 15,000	PVP, A.M.W. 40,000	PVP, A.M.W. 100,000	PVP, A.M.W. 250,000	PVP, A.M.W. 750,000	Sodium carboxymethyl cellulose
0.001	33	35	29	31	26	32
0.005	49	50	35	31	28	38
0.01	55	51	38	33	29	45
0.05	63	64	47	38	36	53
0.1	61	62	53	39	37	

The reflectance of the original cloth sample was 70%.

#### Example II

A standard washing medium was prepared containing: water; sodium alkyl ( $\text{C}_{12}-\text{C}_{18}$ ) benzene sulphonate, 0.12%; and carbon black, 0.1%. The pH was adjusted to 10 by the addition of sodium hydroxide and glycine was added as a buffering agent. To samples of the standard medium were added various concentrations of calcium chloride to furnish media of various hardnesses and to these media were added polyvinylpyrrolidone (concentration 0.01%, average molecular weight 40,000) and sodium carboxymethylcellulose in a concentration of 0.01%. The resulting solutions were used for washing samples of cloth in the same manner as in Example I and the washed swatches were tested in the same manner as aforesaid.

The results are summarized below:

Water hardness, expressed as p.p.m. of $\text{CaCO}_3$	Reflectance of washed samples, expressed in percent	
	PVP, A.M.W. 40,000 conc. 0.01%	Sodium carboxymethylcellulose conc. 0.01%
0	61	51
50	58	48
100	58	48
200	54	35
300	51	18
400	32	24
500	32	16

The reflectance of the original cloth samples was 70%.

Having thus described our invention we claim:

1. A process for removing soil from a textile material and minimizing the re-deposition of removed soil which comprises washing the material with a solution comprising water, an organic surface-active detergent, and polyvinylpyrrolidone.

2. The process of claim 1 wherein the polyvinylpyrrolidone has an average molecular weight from about 15,000 to about 40,000.

3. A washing solution which is effective not only to remove soil from textile materials but also to minimize re-deposition of removed soil comprising water, an organic surface-active detergent, and polyvinylpyrrolidone.

4. The composition of claim 3 wherein the polyvinylpyrrolidone has an average molecular weight from about 15,000 to about 40,000.

5. A composition soluble in water to form a washing solution which is effective not only to remove soil from textile materials but also to minimize re-deposition of removed soil, comprising an organic surface-active detergent and polyvinylpyrrolidone.

6. The composition of claim 5 wherein the polyvinyl-

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pyrrolidone has an average molecular weight of about 15,000 to about 40,000.

7. The composition of claim 5 wherein the detergent is a sodium alkyl benzene sulphonate wherein the alkyl group contains 12 to 18 carbon atoms.

**References Cited in the file of this patent**

**UNITED STATES PATENTS**

2,283,199 Flett ----- May 19, 1942

2,566,501

2,707,959

5 850,328

6

Smith et al. ----- Sept. 4, 1951

Shelanski ----- May 10, 1955

**FOREIGN PATENTS**

Germany ----- Sept. 22, 1952

**OTHER REFERENCES**

Vinyl and Related Polymers, Schildknecht, Wiley and Sons, N.Y. (1952), pages 674-675.