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LIQUID DETERGENT GEL COMPOSITIONS HAVING STABILITY AGAINST SEPARATION

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The present invention relates to liquid detergent gel compositions. The invention likewise relates to detergent compositions which exhibit stability against phase separation and precipitation in the presence of high concentrations of inorganic salts and of synthetic organic detergent components.

In the operation of automatic washing machines and dishwashing machines it is highly desirable to employ liquid detergent concentrates which can be measured and pumped or flowed automatically from a supply tank. Such solutions contain high concentrations of inorganic salts, for example, phosphates and carbonates, in addition to active organic detergent components. The solutions, therefore, readily separate into organic and aqueous phases as well as crystalline precipitates, particularly at low temperatures. Consequently, a pump-feed or gravity system cannot provide a uniform detergent concentrate from such a mixture. In addition the high concentrations of inorganic components, such as phosphates which are desirable for heavy duty purposes, cause crystallization which results in a loss of a part of the detergent composition and also causes plugging of the feed lines.

It has now been found that liquid detergent gel compositions containing an active organic detergent component and inorganic alkaline salts may be stabilized by the combination therewith of a specific stabilizing component.

The stabilizing components employed in the preparation of the present aqueous detergent gels are polyelectrolytes which have been prepared from synthetic, organic, linear polymers by cross-linking. A preferred group of polymers are the vinyl polymers. These include homopolymers, such as those derived from acrylonitrile, and copolymers, such as maleic anhydride copolymerized with an olefinic compound, for example, ethylene, propylene or isobutylene.

A preferred cross-linked vinyl polymer is the reaction product of formaldehyde with hydrolyzed polyacrylonitrile. The hydrolysis of the polyacrylonitrile is carried substantially to completion, such as by alkaline or acid hydrolysis as described in U.S. Patents 2,625,529 and 2,727,835. Other vinyl polymers which have been found to have particular utility in forming cross-linked polymers having stabilizing action in aqueous detergent gels are the copolymers of maleic anhydride. The maleic anhydride is copolymerized in substantially equimolar proportions with other copolymerizable monomers of less than 5 carbon atoms, such as ethylene, propylene, isobutylene, vinyl acetate or vinyl methyl ether. The above maleic copolymers are then cross-linked with a diamine or an alkylene polyamine. The amines employed in this relationship are primary or secondary amines having at least two carbon atoms, for example the alkylene polyamines. The polyamines which have been found to be particularly useful include diethylene triamine, triethylene

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tetramine, tetraethylene pentamine and polyethylene-amine.

The above polymers and copolymers, either before or after cross-linking are transformed into water-swelling forms having utility as stabilizers in the present detergent gels by reaction with a base, such as sodium hydroxide, potassium hydroxide, ammonia or amines. In this way the sodium, potassium, ammonium or amine salts are formed. In order to obtain such salts the copolymers are reacted with the base or an alkylamine, such as methyl, butyl and amylamine, cyclohexylamine or a quaternary ammonium hydroxide, such as phenyl trimethyl ammonium hydroxide. The polymer is thus transformed into the amine or ammonium salt or the half amide.

The above modified polymers may first be cross-linked with a cross-linking agent, such as formaldehyde, a diamine or an alkylene polyamine to obtain a gel-forming stabilizing agent containing a small amount of cross-linking product by the above cross-linking agents. The cross-linking in the molar structure are due primarily to amide linkages. The formaldehyde cross-linking reaction is primarily through residual amide groups in the hydrolyzed or partially hydrolyzed polymer, for example, polyacrylonitrile. Another way of preparing effective liquid detergent gel stabilizers is to begin with polyacrylamide which is utilized as a pure homopolymer for cross-linking with formaldehyde to obtain a gel-forming material.

The cross-linking of the above-described synthetic, organic linear polymers results in the production of a water-swelling, gel-forming material which is of utility in the manufacture of the present aqueous detergent gels. The degree of cross-linking, as defined herein, is the percent by weight of the cross-linking agent, such as the above formaldehyde or alkylene polyamine based upon the weight of the original polymer.

Hydrolyzed polyacrylonitrile which has been cross-linked with formaldehyde has been found to give particularly effective aqueous detergent gels when the range of formaldehyde employed is from 0.01% to 0.30% by weight of formaldehyde relative to the hydrolyzed polyacrylonitrile. A more preferred range is from 0.01% to 0.20% by weight of formaldehyde. Acetaldehyde may similarly be used in cross-linking the hydrolyzed polyacrylonitrile to obtain a gel-forming polyelectrolyte. The cross-linked polyelectrolytes may be employed as various basic salts, such as the sodium, potassium, ammonium, or basic amine salts. The preferred salt is the sodium salt. An example of such an amine salt is the isobutylamine salt.

The gel-forming polyelectrolytes employed as stabilizing agents in the present invention are characterized in having viscosities in the range of 100 to 10,000 centipoises or more preferably from 1,000 to 8,000 centipoises (Brookfield, 6 r.p.m.) measured on a solution containing 1.0 weight percent of the material in water. For example, a preferred type of sodium salt of the formaldehyde-cross-linked polymer of hydrolyzed polyacrylonitrile has a viscosity of about 6,000 centipoises and a gel of isobutylene-maleic anhydride cross-linked with ethylene diamine, and employed as the ammonium salt as a viscosity of 1,500 centipoises.

The proportion of the cross-linked vinyl polymer employed in the present aqueous detergent gel compositions is from 0.25% to 2.0% by weight of the said cross-linked

vinyl polymer in the total detergent gel composition. A preferred range is from 0.75% to 1.25% by weight.

The active detergent components employed in the present invention are synthetic, organic detergents, preferably of the non-ionic type. However, minor proportions of other active detergent components such as the alkaline salts of alkylaryl sulfonic acids may also be employed in the present invention.

In the practice of the present invention, preferred non-ionic detergent components include alkylene oxide condensation products of highly branched monohydric primary alcohols having the molecular configuration of an alcohol produced by the Oxo process from olefins of the class consisting of polybutylenes and polypropylenes such as triisobutylene, tetrapropylene, tetraisobutylene, pentapropylene, pentaisobutylene and hexapropylene. These condensation products may contain on the average of from 1 to 20 moles, preferably from 5 to 15 moles of condensed alkylene oxide per mole of the said alcohol. The alkylene oxides employed have from 2 to 3 carbon atoms. The condensation products may also be made with combinations of alkylene oxides, such as by condensing isodecyl alcohol with 8 moles of propylene oxide, followed by 6 moles of ethylene oxide.

When polymer olefins such as polyisobutylene or polypropylene are reacted according to the Oxo reaction with carbon monoxide and hydrogen in the presence of a catalyst containing cobalt carbonyl, and the reaction products hydrogenated, a mixture of isomeric alcohols having a wide boiling range is obtained. The alcohols may be manufactured by the process described in Bureau of Mines Report of Investigation No. 4270, dated June 1948. In view of the presence of a number of isomers of triisobutylene or tetrapropylene, for example, in the polymer olefins which are treated according to the Oxo reaction and furthermore, since there is considerable isomerization, polymerization and depolymerization of the olefins due to the catalytic action, the resulting alcoholic product contains a large number of different alcohols, some of which are polyhydric alcohols. By reason of the large number of compounds present in the Oxo reaction product it has so far been impossible to ascertain the exact composition of this product. It has been found, however, that the fraction consisting substantially only of tridecyl alcohols boiling within the range 226° C. to 264° C. (ASTM distillation at atmospheric pressure) may be reacted with ethylene oxide to obtain mixed polyethers which have outstanding properties as a detergent component in the present invention.

Another preferred class of synthetic, organic detergents which may constitute all or part of the active component in the present aqueous detergent gels includes alkylene oxide condensation products of other hydroxy organic compounds such as alkylphenols. Preferred alkylphenols are those having alkyl radicals of from 8 to 18 carbon atoms. The condensation products of the said alkylphenols are prepared with an alkylene oxide having from 2 to 3 carbon atoms, e.g., a condensation product may be prepared by first using ethylene oxide, and then further condensing with propylene oxide, or vice versa. Preferred condensation products of this type contain from 5 to 25 alkylene oxide groups per mole of the said alkylphenols, for example 7 moles of ethylene oxide condensed with one mole of nonylphenol.

Other detergent components may supplement the above-described components in the present detergent concentrates. Typical of these types of detergents are the alkylolamides having from 10 to 20 carbon atoms in the acid radical. The alkylolamides may be derived from fatty acids such as those obtained from coconut oil glycerides. The alkylolamides are therefore technical products containing a range of fatty acid radicals, but may be considered as representative of lauric acid. Another source is the tall oil fatty acids, which may be obtained by distillation from tall oil. The alkylolamide is formed by

the reaction of the above fatty acids with an alkylolamine such as mono- or diethanolamine, mono- or diisopropanolamine, or mono- or di-n-propanolamine.

Another group of auxiliary detergent components which may be employed in the present invention is the class of aromatic sulfonates such as the sodium sulfonates of an alkylated aromatic hydrocarbon. These sulfonates may be prepared by condensing an aliphatic hydrocarbon having from 9 to 18 carbon atoms, with an aromatic hydrocarbon selected from the class consisting of benzene, toluene, and xylene, and thereafter sulfonating the product and neutralizing it to obtain the sodium, ammonium or alkylammonium salt. The preferred aromatic hydrocarbon member of this group is benzene, but the compounds obtained from toluene and xylene have also been found to have desirable properties as surface-active compositions. The alkyl group is preferably of about 10 to 12 carbon atoms average length, such as may be obtained from olefin polymers or kerosene. An olefin-polymer alkylate composition of this type is produced by alkylating the aromatic hydrocarbon, with an olefin hydrocarbon averaging 9 to 18 carbon atoms in the molecule, and thereafter sulfonating and neutralizing the product. When kerosene is employed as the source of the alkyl groups, the kerosene may be chlorinated and the aromatic compound alkylated therewith in known manner. Such compounds are described in U.S. 2,232,117 and U.S. 2,232,118 to Kyrides.

In the formulation of the present aqueous detergent gels, a major component is an alkaline material selected from the group consisting of inorganic phosphates, carbonates, silicates and combinations thereof. The said organic salts are preferably potassium salts, although sodium salts may also be employed, particularly in combination with the potassium salts. The phosphate compounds must be chain polyphosphates. Such polyphosphates contain more than one phosphorus atom per molecule, as distinguished from orthophosphates which contain only one phosphorus atom per molecule. Chain polyphosphates are non-cyclic (and usually linear) phosphates, as distinguished from ring or cyclic phosphates such as trimetaphosphate and tetrametaphosphate. Examples of the more common chain polyphosphates are tetrapotassium pyrophosphate and potassium tripolyphosphate, both of which can be obtained as essentially pure crystalline materials, and an amorphous polyphosphate known as potassium hexametaphosphate or sodium hexametaphosphate.

The amorphous polyphosphates, also known as glassy phosphate, are generally characterized either in terms of mole ratio of K_2O (or Na_2O) to P_2O_5 , or in terms of average chain length, \bar{n} , of the polyphosphate molecules in the glassy phosphate. For example, commercial sodium hexametaphosphate has a mole ratio of Na_2O to P_2O_5 of about 1.13, and an average chain length of about 15 phosphorus atoms. In general, any of the water-soluble glassy polyphosphates, which have mole ratios of Na_2O or K_2O relative to P_2O_5 ranging between about 5:3 and about 1:1 (corresponding to a range of average chain length from 3 to several thousands or higher) are suitable for use as the chain polyphosphate ingredient of the present aqueous detergent gels.

Another ingredient which is preferably utilized along with the above-described detergent compounds and chain-polyphosphates in the aqueous detergent solutions prepared according to this invention are the water-soluble sodium and potassium silicates. As is well known, sodium silicates can vary quite widely in composition, ranging from tetra- and disilicates having a mole ratio of $Na_2O:SiO_2$ of 1:4 and 1:2, respectively, to the more alkaline silicates, such as the orthosilicate having a mole ratio of $Na_2O:SiO_2$ of 2:1. In general, potassium silicate ($K_2O:SiO_2=1:2.1$) is the preferred compound silicate for use according to the present invention. However, other silicates, or mixtures of silicates, have an overall mole ratio of $Na_2O:SiO_2$ between about 1:1 and 1:4.

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The carbonates employed are preferably the potassium carbonates such as commercial pearl ash or modified potassium carbonates having various degrees of alkalinity. Minor amounts of additional ingredients, such as borax and potassium or ammonium borates, dyes, perfumes, etc., can also be incorporated into the liquid detergent. Additionally, the ultimate concentrate mixture is preferably formulated so that an aqueous solution of about 0.25 weight percent has a pH of between about 8 and about 11.

In making up concentrated detergent liquid gels according to the present invention, the aforementioned said ingredients should be utilized in the following proportions: (1) 5% to 25% by weight of active detergent compounds; (2) from 10% to 50% of chain polyphosphate; (3) from 1% to 10% of water-soluble silicate (calculated on the basis of anhydrous material); and from 0.25% to 2.0% of the cross-linked polymer as the gel stabilizer.

The liquid formulations of the present invention contain from 30% to 75%, and preferably from 40% to 65% by weight of water based upon the total liquid detergent. Alcohols, such as ethanol and glycols, such as ethylene glycol or propylene glycol may also be employed in the present detergent compositions, particularly to improve the compatibility of the various components over a wide range of temperature conditions. The proportion of alcohol or glycol may be from 1% to 20% by weight.

The present products have been found to be of particular utility in automatic washers as a liquid concentrate, which is readily pumped through pipes and tubing into the washing chamber. These compositions may be stored for prolonged periods of time without separation into organic and inorganic layers. This is essential in the production of a liquid detergent which is to be utilized in small increments during a long period of storage.

The following examples illustrate specific embodiments of the invention.

Example 1

A detergent gel product was prepared by mixing the following components in parts by weight:

Condensation product of 8.5 moles of ethylene oxide with 1 mole of tridecanol	15
Potassium tripolyphosphate	30
Carboxymethylcellulose (0.7 degree of substitution)	1.5
Sodium salt of formaldehyde-cross-linked hydrolyzed polyacrylonitrile	1.0
Water	52.5

This detergent product was found to be stable in storage without phase separation. In contradistinction, the same basic formulation without the sodium salt of formaldehyde-cross-linked hydrolyzed polyacrylonitrile exhibited phase separation five minutes after mixing.

In the above formulation the carboxymethylcellulose (0.7 degree of substitution) is employed as a soil-suspending agent, which prevents redeposition of the soil removed from fabrics, etc. The reference 0.7 degree of substitution indicates the degree of carboxymethylation of the cellulose, i.e., there are 0.7 carboxymethyl groups per anhydroglucose unit of the cellulose. Carboxymethylcellulose when used in the above formulation without the sodium salt of formaldehyde cross-linked hydrolyzed polyacrylonitrile has been found to be without stabilizing action as required in the present high concentration liquid detergents.

In the present combination detergent it has been found that the stabilizing components such as the cross-linked reaction product of formaldehyde with hydrolyzed polyacrylonitrile also aids in the dispersion of the carboxymethylcellulose, which ordinarily is very difficult to incorporate into a built liquid detergent.

The following detergent compositions were prepared as further examples of high concentration liquid detergent

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gels stabilized by the presence of cross-linked polymers (proportions by weight).

Example 2

	Percent
Condensation product of 8.5 moles of ethylene oxide with 1 mole of tridecanol	13.5
Isopropanolamide of lauric acid	1.5
Potassium tripolyphosphate	30.0
Carboxymethylcellulose (0.7 degree of substitution)	1.5
Sodium salt of formaldehyde-cross-linked hydrolyzed polyacrylonitrile	1.0
Water	52.5

The above composition was found to be stable for a period of 20 days when given an accelerated deterioration test at 50° C. The composition did not crystallize out nor exhibit any phase separation.

Example 3

	Percent
Condensation product of 8.5 moles of ethylene oxide and 3.0 moles of propylene oxide with 1 mole of tridecanol	8.5
Sodium salt of sulfonated dodecylbenzene	5.0
Isopropanolamide of lauric acid	1.5
Potassium tripolyphosphate	30.0
Carboxymethylcellulose (0.7 degree of substitution)	1.5
Sodium salt of formaldehyde-cross-linked hydrolyzed polyacrylonitrile	1.0
Water	52.5

The above formulation was found to be stable for a period of 13 days in an accelerated stability test conducted at 50° C.

Example 4

	Percent
Condensation product of 4 moles of propylene oxide and 10 moles of ethylene oxide with 1 mole of tridecanol	15.0
Potassium tripolyphosphate	6.25
Sodium tripolyphosphate	6.25
Potassium carbonate	15.0
Potassium silicate (1:2.1 K ₂ O:SiO ₂ ratio)	2.75
Carboxymethylcellulose (0.7 degree of substitution)	0.75
Sodium salt of formaldehyde-cross-linked hydrolyzed polyacrylonitrile	1.0
Gel of cross-linked polymer of isobutylene-maleic anhydride (1:1 molar proportion)	0.5
Water	52.5

The above composition was tested against phase separation at 50° C. and was found to be stable for a period of 13 days.

Example 5

	Percent
Condensation product of 12 moles of ethylene oxide with 1 mole of tall oil	15.0
Potassium tripolyphosphate	30.0
Sodium salt of formaldehyde-cross-linked hydrolyzed polyacrylonitrile	1.25
Water	53.75

The above detergent concentrate was stable at a 50° C. temperature for a period of six days.

Example 6

In order to demonstrate the inadequacy of conventional carboxymethylcellulose as a stabilizer for liquid detergent compositions of high concentration, the following composition was prepared:

	Percent
Condensation product of 8.5 moles of ethylene oxide with 1 mole of tridecanol	15.0
Potassium tripolyphosphate	30.0
Carboxymethylcellulose (0.7 degree of substitution)	3.0
Water	52.0

The above mixture, when subjected to the conventional agitation as utilized in the foregoing examples was found to separate immediately into an aqueous and organic phase.

Example 7

	Percent
Condensation product of 7.7 moles of ethylene oxide with 1 mole of nonyl-phenol -----	15.0
Potassium tripolyphosphate -----	12.5
Potassium carbonate -----	15.0
Potassium silicate (1:2.1 K ₂ O:SiO ₂ ratio) -----	2.5
Carboxymethylcellulose (0.7 degree of substitution) -----	0.75
Sodium salt of formaldehyde-cross-linked hydrolyzed polyacrylonitrile -----	1.25
Water -----	53.0

The above detergent composition is intended particularly as an easily pumpable concentrate for dishwashing machines. This composition was found to be stable for a period of five days in a phase separation test conducted at 50° C.

What is claimed is:

1. An aqueous liquid detergent gel consisting essentially of 40% to 65% by weight of water and 5% to 25% of a synthetic, non-ionic, organic detergent compound in combination with 10% to 50% of an alkaline substance selected from the group consisting of sodium and potassium chain polyphosphates, silicates and combinations thereof together with 0.25% to 2% of a cross-linked vinyl polymer having a viscosity of from 100 to 10,000 centipoises.

2. An aqueous liquid detergent gel consisting essentially of 40% to 65% by weight of water and 5% to 25% of a synthetic, non-ionic, organic detergent compound in combination with 10% to 50% of an alkaline material selected from the group consisting of sodium and potassium chain polyphosphates, silicates and combinations thereof together with 0.25% to 2% of a cross-linked vinyl polymer having a viscosity of from 1,000 to 8,000 centipoises.

3. An aqueous liquid detergent gel consisting essentially of 40% to 65% by weight of water and 5% to 25% of a synthetic, non-ionic, organic detergent compound in combination with 10% to 50% of an alkaline substance selected from the group consisting of sodium and potassium chain polyphosphates, silicates and combinations thereof together with 0.75% to 1.25% of a cross-linked vinyl polymer having a viscosity of from 100 to 10,000 centipoises.

4. An aqueous liquid detergent gel consisting essentially of 40% to 65% by weight of water and 5% to 25% of a synthetic, non-ionic, organic detergent compound in combination with 10% to 50% of an alkaline material selected from the group consisting of sodium and potassium chain polyphosphates, silicates and combinations thereof, together with 0.75% to 1.25% of a cross-linked vinyl polymer having a viscosity of from 1,000 to 8,000 centipoises.

5. An aqueous liquid detergent gel consisting essentially of 40% to 65% by weight of water and 5% to 25% of a synthetic, non-ionic, organic detergent compound in combination with 10% to 50% of an alkaline material selected from the group consisting of sodium and potassium chain polyphosphates, silicates and combinations thereof, together with 0.25% to 2% of a sodium salt of formaldehyde-cross-linked hydrolyzed polyacrylonitrile having a viscosity of from 100 to 10,000 centipoises.

6. An aqueous liquid detergent gel consisting essentially of 40% to 65% by weight of water and 5% to 25% of a synthetic, non-ionic organic detergent compound in combination with 10% to 50% of an alkaline material selected from the group consisting of sodium and potassium chain polyphosphates, silicates and combinations thereof, together with 0.25% to 2% of a potassium salt

of formaldehyde-cross-linked hydrolyzed polyacrylonitrile having a viscosity of from 100 to 10,000 centipoises.

7. An aqueous liquid detergent gel consisting essentially of 40% to 65% by weight of water and 5% to 25% of a synthetic, non-ionic organic detergent compound in combination with 10% to 50% of an alkaline material selected from the group consisting of sodium and potassium chain polyphosphates, silicates and combinations thereof, together with 0.25% to 2% of a polymer of isobutylene and maleic anhydride cross-linked by reaction with an alkylene polyamine, and having a viscosity of from 100 to 10,000 centipoises.

8. An aqueous liquid detergent gel consisting essentially of 40% to 65% by weight of water and 5% to 25% of a synthetic, non-ionic, organic detergent compound in combination with 10% to 50% of an alkaline material selected from the group consisting of sodium and potassium chain polyphosphates, silicates and combinations thereof, together with 0.25% to 2% of a polymer of ethylene and maleic anhydride, cross-linked by reaction with an alkylene polyamine, and having a viscosity of from 100 to 10,000 centipoises.

9. An aqueous liquid detergent gel consisting essentially of 40% to 65% by weight of water and 5% to 25% of a synthetic, non-ionic, organic detergent compound in combination with 10% to 50% of an alkaline material selected from the group consisting of sodium and potassium chain polyphosphates, silicates and combinations thereof, together with 0.25% to 2% of a polymer of isobutylene and maleic anhydride, cross-linked by reaction with ethylene diamine, the said cross-linked polymer having a viscosity of from 100 to 10,000 centipoises.

10. An aqueous liquid detergent gel consisting essentially of 40% to 65% by weight of water and 5% to 25% of a synthetic, non-ionic, organic detergent compound in combination with 10% to 50% of an alkaline material selected from the group consisting of inorganic sodium and potassium chain polyphosphates, silicates and combinations thereof, together with 0.25% to 2% of a polymer of ethylene and maleic anhydride, cross-linked by reaction with ethylene diamine, the said cross-linked polymer having a viscosity of from 100 to 10,000 centipoises.

11. A phase stable detergent composition having the following approximate proportions as parts by weight:

Condensation product of 8.5 moles of ethylene oxide with 1 mole of tridecanol -----	15
Potassium tripolyphosphate -----	30
Carboxymethylcellulose, sodium salt, 0.7 degree of substitution -----	1.5
Sodium salt of formaldehyde-cross-linked hydrolyzed polyacrylonitrile -----	1.0
Water -----	52.5

12. A phase stable detergent composition having the following approximate proportions as parts by weight:

Condensation product of 8.5 moles of ethylene oxide and 3.0 moles of propylene oxide with 1 mole of tridecanol -----	8.5
Sodium salt of sulfonated dodecylbenzene -----	5.0
Isopropanolamide of lauric acid -----	1.5
Potassium tripolyphosphate -----	30.0
Carboxymethylcellulose, sodium salt, 0.7 degree of substitution -----	1.5
Sodium salt of formaldehyde-cross-linked hydrolyzed polyacrylonitrile -----	1.0
Water -----	52.5

13. A phase stable detergent composition having the following approximate proportions as parts by weight:

Condensation product of 8.5 moles of ethylene oxide with 1 mole of tridecanol -----	13.5
Isopropanolamide of lauric acid -----	1.5
Potassium tripolyphosphate -----	30.0

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Carboxymethylcellulose, sodium salt, 0.7 degree of substitution -----	1.5	
Sodium salt of formaldehyde-cross-linked hydrolyzed polyacrylonitrile -----	1.0	
Water -----	52.5	5

2,645,615

889,373

896,430

650,222

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Pollok ----- July 14, 1953

FOREIGN PATENTS

France ----- Oct. 4, 1943

France ----- Apr. 24, 1944

Great Britain ----- Feb. 21, 1951

References Cited in the file of this patent

UNITED STATES PATENTS

2,560,839	Aye -----	July 17, 1951
2,621,169	Robinette -----	Dec. 9, 1952

OTHER REFERENCES

Schwartz and Perry: "Surface Active Agents," Interscience Publishers, Inc., N.Y. (1949), page 204.