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# STARCH-FLUORO POLYMER TEXTILE SIZING, WATER AND OIL REPELLENT COMPOSITION

Robert Tweedy Hunter, Jr., Mendham, and Herman Lowell Marder, Plainfield, N.J., assignors to Colgate-Palmolive Company, New York, N.Y.

No Drawing. Continuation of abandoned application Ser. No. 740,437, June 19, 1968. This application Feb. 4, 1972, Ser. No. 223,735
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U.S. Cl. 260—17.4 ST 6 Claims

## ABSTRACT OF THE DISCLOSURE

A textile sizing, i.e., starching, composition which also imparts a measure of water and/or oil-repellency containing a water-soluble starch and a fluoropolymer emulsion dispersed, preferably, under the aegis of normally gaseous propellant.

This is a continuation, of application Ser. No. 740,437, filed June 19, 1968, and now abandoned.

The present invention relates to a new and outstanding textile treating composition and particularly to compositions of the type normally used preparatory to ironing textiles. The compositions serve primarily to size and impart water- and oil-repellency. By sizing is meant the ability to stiffen the textile and in many instances to add gloss to the textile surface.

The use of starch as a size and stiffening agent for textile materials is probably as old as textile themselves. It is only within the last several decades that the housewife has been offered such a product in an already prepared liquid form for application to the textile before ironing. Such starching compositions are now available in a variety of forms and among the most popular is an aerosol-type formulation.

It is well known that in order to obtain a desirable stiffening of the textile material after washing, it is necessary after each washing and before each ironing to treat the textile with the starching composition. Obviously, this is so because of the non-durable nature of the sizing compositions used. As a practical matter, it is necessary that the sizing, i.e., starching composition, be non-durable and produce no build-up of stiffening action from one wash to another since this would lead to stiffening of the textile material to an undesirable degree in most instances. By virture of the non-durable characteristics of the conventional starching compositions, it is possible for the housewife to control the degree of size and stiffening with each product at any given time.

It is also known to treat textile materials with various water- and/or oil-repellent compositions, and usually such operations are carried out in the mill during the manufacture of the base textile material although it is not by any means uncommon to find products which can be used for such purposes by the housewife and which are in fact so used on an individual basis to produce a water repellent or an oil repellent finish on the textile material. The products normally employed for producing water repellency and/or oil repellency do not produce any stiffening or sizing action on the textile. However, such compositions which have in fact combined a starch formulation with an oil and/or water repellency producing material has resulted in a formulation with strong durability characteristics for the oil and water repellency portion of the formulation. Clearly, a build-up of such a material will produce undersirable features.

The present invention provides a sizing or stiffening composition, i.e., a starch composition, which not only produces the desired degree of size and stiffness, which not only affords control by the consumer of these characteristics by virtue of the non-durability between washings of this finish, but also provides water and oil repellency which is non-durable in nature.



The compositions of the present invention comprise as the essential ingredients thereof, a water soluble or water dispersible sizing material, which is a polysaccharide as exemplified by the various natural starches and the various starch derivatives such as oxidized starches, acylated starches, starch ether, hydrolyzed starches, enzyme-treated starches and the like. The starch composition is in combination with a thermoplastic film-forming fluorocarbon polymer as hereinafter described. In addition to the starch and fluoro polymer there may also be present in the compositions of this invention many other additives which do not adversely affect the attainment of non-durable stiffening along with non-durable water and oil repellency. Examples of such additional materials include anti-stick agents such as the siloxane resins, polyethylene and the like; additional water repellent materials such as long chain fatty quaternary ammonium compounds; anti-oxidants; anti-foamers; stabilizers; bacteriacides; surface active agents; coloring materials; perfumes; textile fiber-reactive chemicals, e.g., formaldehyde, glyoxal; crease resistant and crease proofing agents, and the like.

The preferred form of the compositions of this invention is a self-propelling liquid composition wherein the major carrier liquid is water and the propellant is a suitable low boiling hydrocarbon or halogenated hydrocarbon as exemplified by methylchloride, methylenechloride, isobutane and the various chlorinated fluorinated methanes, ethanes, and the like, such as dichlorodifluoro methane and the like.

The non-durable size or stiffening component is preferably selected from the general class of starches and starch derivatives and among these the most preferred material is an acetylated amylopectin which is a thin boiling cook-up type starch and is illustrative of the preferred class of products of high fluidity, i.e., 30 to 100 (intrinsic viscosity of from 1.0 to 0.3). Other starch products which may be employed include the following: gelatinized rice starch, gelatinized tapioca ethoxylated starch, gelatinized carboxymethyl starch, nitrogenated starch, oxidized corn starch, alkylated starch, dextrins and the like.

The amount of starch material which may be employed in the compositions of this invention may be varied widely, but in general from about 1% to about 10% thereof based on the total weight of the aerosol formulation may be used. More important than the specific amount of size material, is the ratio of the latter to the fluorocarbon polymer employed. In general, the ratio of these two components may vary from about 1:2 to 100:1 (size to fluoro polymer) and within this range it is preferred to employ a ratio of from about 2:1 to 20:1. By the use of the aforementioned ratios and, particularly, the narrower range, it has been found that an outstanding non-durable stiffening action is obtained which does not interfere with the provision of excellent repellent characteristics.

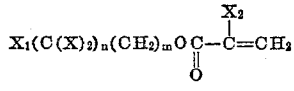
The fluoropolymer component of the compositions of this invention comprise a thermoplastic polymeric material having a molecular weight of less than 30,000 in the form of an emulsion, known as a latex, which is characterized by the ability to dry to a continuous cohesive film. Fluoro polymers are well known but those which are preferred from monomers in the present invention comprise the general class of the perfluoro acrylates and alpha-substituted acrylates, such as methacrylates, all having in common the fact that they are of a low molecular weight. Such fluoro polymers are prepared from the corresponding monomers but include a chain transfer agent, e.g., alkanethiol, such as dodecyl mercaptan, to terminate the polymer. As illustrative of the fluoro polymers which

may be used in the present invention, mention may be made of the following:

Homipolymers of:

1H,1H-perfluorohexyl acrylate
1H,1H-perfluorocetyl acrylate
1H,1H-perfluorodecyl acrylate
1H,1H-perfluorododecyl acrylate
1H,1H-perfluorohexyl methacrylate
1H,1H-perfluorodecyl methacrylate
1H,1H-perfluorododecyl methacrylate
1H,1H-perfluorohexyl-α-fluoroacrylate
1H,1H-perfluorodecyl-α-fluoroacrylate
1H,1H,7H-perfluoroheptyl acrylate
1H,1H,11H-perfluoroundecyl methacrylate
1H,1H,11H-perfluoroctyl acrylate
1H,1H,3H-perfluorooctyl-α-fluoroacrylate
1H,1H-perfluoroheptyl-α-chloroacrylate

the general formula of which may be presented as follows:



wherein $X_1$ is hydrogen, chlorine or fluorine; X is hydrogen, alkyl ($C_1$ to $C_8$) chlorine or fluorine, $n$ has a value of 3 to 30, $m$=1, 2 or 3. $X_2$ is hydrogen, lower alkyl ($C_1$ to $C_4$) or halogen and at least 70% but not less than 6 of the X's are fluorine; interpolymers (i.e., copolymers and terpolymers of the aforementioned monomers; with polymerizable vinyl compounds, said interpolymer containing at least 25 mole percent of fluoro monomer.

Suitable comonomers include:

vinyl esters of organic and inorganic acids, e.g., vinyl chloride; vinyl bromide; vinyl fluoride; vinyl acetate; vinyl propronate; vinyl stearate; vinyl benzoate;
vinyl ethers, e.g., methyl vinyl ether; ethyl vinyl ether; n-butyl vinyl ether; decylvinyl ether; octadecyl vinyl ether; benzyl vinyl ether; phenyl vinyl ether; and divinyl ether;
alkyl vinyl ketones (alkyl $C_1$ to $C_{30}$)
alkyl acrylates (alkyl $C_1$ to $C_{30}$)
alkyl methacrylates (alkyl $C_1$ to $C_{30}$)
vinylidene halides
acrylic acid
acrylonitrile
acrylamide
N-methylol acrylamide; N-methoxy methyl acrylamide
styrene, alkyl styrenes
1,3-butadiene
alkyl esters
alkyl halides
mono- and di-acrylate esters of alkanediols
mono- and di-vinyl esters of alkanedieic acids

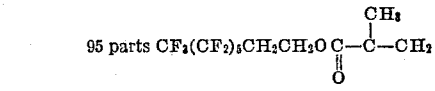
and the like.

It is of primary importance to the practice of the invention to achieve non-durability of the fluoro polymer by utilizing a low molecular weight fluoro polymer latex which dries by itself to a brittle film.

Other resin emulsions may be added to the compositions of this invention to give special benefits. Thus, one may add minor amounts (up to about 300% of the weight of fluoro polymer) based on the weight of the total composition of any of the aforementioned fluorinated polymers among others, e.g., acrylic emulsions, such as Rhoplex B–15, poly 1,3-dichlorobutadiene, polysiloxane emulsions, polyethylene emulsions, polybutadiene emulsions, polystyrene emulsions, and the like.



A typical low molecular weight fluoro polymer product is prepared from the following: (polymerization run at 70° C. for 5 hours).



2 parts n-butyl acrylate
2 parts octadecyl dimethylamine acetate
1.2 parts dodecyl mercaptan
200 parts water

The polymer produced by this technique is of much lower molecular weight than that normally prepared in the absence of the chain transfer agent, namely, dodecyl mercaptan.

The formulations of the present invention may be used in any convenient concentration in a bath spray, roller padder or aerosol method of application. Generally concentrations are selected to give a solid pick-up based on the material treated of between 0.1 to 10% by weight. Since in order to obtain uniform treatment of a textile, it is desirable to have from about 1% to 200% and preferably from about 25% to 100% wet pick-up the concentrations of active components in the treating composition for the preferred pick-up will vary from about 40% down to 0.1%. Clearly, such concentrations are not critical and are subject to the wide variation and great latitude indicated above.

In the preferred and most convenient method of application by the consumer of the composition of this invention, i.e., aerosol method, the aqueous compositions are formulated with a suitable propellant. These include trichloromonofluoromethane, dichlorotetrafluoroethane, dichloromonofluoromethane, monochlorotrifluoromethane, rochloroethane, 1,1,1-cyclobutane, carbondioxide, nitrous oxide.

In general the propellants are water-immiscible or only slightly soluble in water with vapor pressures at 70° F. of from about 0.2 to about 500 p.s./g. The selection of a suitable propellant or mixture of propellants will, of course, depend on the type of package to be used, the specific nature of the composition to be dispensed, and the spray pattern desired, among others. Where lower pressures are to be maintained in the package it may be desirable to use a propellant of slight water solubility to aid in dispensing the product after it leaves the nozzle.

The preferred propellants are the low density compounds and mixtures of low density which form a separate and upper liquid phase in the aerosol package providing thereby a separate phase system. While it is not intended to foreclose the use of higher density propellants (i.e., higher than the aqueous latex phase) in which case the propellant will be on the bottom in the aerosol package, this is not preferred because of the inadequacies of the mechanics of the package required for dispensing such compositions and further because other means for making such systems workable (i.e., shortened dip tube) create undesirable economic factors (e.g., cannot discharge a high percent of the active ingredients). In order to achieve the benefits of this invention, however, any technique aerosol or otherwise may be employed notwithstanding the fact that the optimum results may be obtained with certain specific formulations and techniques and these might, in general, be preferred especially by the housewife.

The amount of propellant as well as the specific one or ones used will vary depending upon the pressure limitations on the package and the spray pattern desired. Generally from 3% to 25% by weight of propellant circumscribes the practical range thereof, and as pointed out above, among these the low density, medium vapor pressure hydrocarbons such as isobutane are preferred.

As previously pointed out many other adjuvants may be used in the compositions of this invention, some with

particularly noteworthy results. Thus incorporation of a polyethylene emulsion or poly 1,3-dichlorobutadiene emulsion in amounts ranging from 10% to 300% by weight based on the weight of fluoropolymer gives rise to unique ironing characteristics to textiles sprayed with such modified embodiments as will be seen hereinafter.

The following examples serve to illustrate the present invention without being deemed limitative thereof. Parts are by weight unless otherwise indicated.

## EXAMPLE I

A composition is prepared of the following components:

2.7% acetylated amylopectin (thin boiling starch characterized by a viscosity of 14.4 cps. or a 5% solution in water measured at 76° F., pH=5.2)

0.3% copolymer produced from the following:

(a) 1H,1H,2H,2H - tridecafluorooctyl methacrylate (97%)

(b) n-butyl acrylate (2%)

(c) dodecyl mercaptan (1%)

Balance water

A sample of cotton fabric is immersed in the above aqueous composition squeezed to 50% pick-up, air dried until slightly damp and ironed at 400° F. to dryness. The resultant fabric exhibits good water- and oil-repellency and has a crisp handle characteristic of a starched material.

## EXAMPLE II

20 parts acetylated amylopectin (National 1135 starch)
1 part chain terminated copolymer as a 25% solids latex as produced at (A) above.

The resultant was compounded to produce an aqueous formulation of 10% starch, 5% fluoro polymer, 7% isobutane as the propellant.

## EXAMPLES III TO VII

In these examples a basic starch containing preparation is prepared by cooking 3.2 grams of National Starch Company's No. 1135 in approximately 500 grams of deionized water for approximately 15 minutes. The solution was allowed to cool to room temperature and 1 gram of 37% formaldehyde solution was added, for preservative purposes, and the entire batch was diluted with cool, deionized water to a final weight of 640 grams.

80 gram portions of this starch concentrate were used in formulation of aerosol preparations in accordance with these examples. The final weight of each formulation was 150 grams. The propellant was isobutane so that it comprised 7% isobutane. The formulations had various additives incorporated therewith as set forth below wherein the starch is equivalent to 2.6% starch solids in the final formulation and the other ingredients are as indicated:

TABLE I

| | Percent | | |
|---|---|---|---|
| Example | Starch | Fluoro polymer | Non-fluorinated polymer |
| III | 2.67 | 0.3 | 0.6 acrylic emulsion. |
| IV | 2.67 | 0.3 | 0.6 poly 1,3-dichlorobutadiene emulsion. |
| V | 2.67 | 0.3 | 0.6 polyethylene emulsion. |
| VI | 2.67 | 0.3 | |
| VII | 2.67 | | |

Example VIII is considered a control so that in the following test method the tested swatches were not treated.

The fluoro polymer in the above was of the low molecular weight type produced in accordance with A in the above.

The acrylic emulsion used in Example III is further identified as Rhoplex B–15, a product of Rohm and Haas Co.

The aerosol preparations of Examples III to VII are used in the uniform spraying to wetness of white cotton swatches having an 80 x 80 count so that there is a 50% wet pick up. The swatches are heat cured in a conventional manner as by ironing at 400° F. at a rate of about 33 seconds/foot$^2$ to dryness.

Several tests can be employed to establish the effectiveness of the present process for imparting water repellent and oil repellent properties to the various substrates employing the formulations produced in Examples III to VII.

While a number of tests have been devised to determine the degree of stain resistance of fabrics and the subsequent launderability thereof, many of the tests fail by reason of the difficulty of making such tests consistently reproducible. Colgate-Palmolive research scientists have developed an ingenious test system which overcomes the shortcomings of the previous tests. Essentially, their method consists of placing onto the fabric measured volumes of standard common staining materials and comparing the size and intensity to a visual standard. In this way a semi-quantitative estimation of the staining characteristics of a given fabric is obtained.

The test technique employs three water borne stains, namely, (1) chocolate milk, (2) black coffee, and (3) imitation "Coke"; and three oil borne stains, namely, (4) flue dyed corn oil, (5) French dressing, and (6) blue dyed petroleum oil.

The staining materials mentioned in the above have the following compositions:

1. Chocolate milk stain

| | Cc. |
|---|---|
| Evaporated milk | 80 |
| Corn syrup | 20 |
| Chocolate syrup | 20 |
| Water | 60 |

This stain should be prepared once a week and kept refrigerated.

2. Black coffee

| | G. |
|---|---|
| Instant coffee | 1.5 |
| Boiling water | 98.5 |

The coffee solution is allowed to cool until it reaches 70–80° F. The stain should not be kept for more than eight hours.

3. Imitation "Coke"

| | Cc. |
|---|---|
| "Coke" syrup | 50 |
| Isopropanol | 50 |
| Water | 100 |

4. Blue dyed corn oil

0.40 g. blue dye is added to 400 g. corn oil with stirring and heat in order to obtain a uniform solution.

5. French dressing

Once a bottle is opened, it should be stored in a refrigerator.

6. Blue dyed petroleum oil

250 g. of oil are mixed with 0.1% blue dye by weight of the oil. The mixture is agitated and warmed in order to obtain a uniform solution.

The test in the instant case is a static stain repellency test in that the fabric surface is given a minimum disturbance.

In application the temperature of the stain materials is between 70–80° F. A piece of white fabric approximately 7 inches by 7 inches is placed on blotting paper on a hard surface. 1½ cc. of each test stain is carefully placed (not dropped) in separate areas on the fabric. After two minutes, the excess stain material, if any, is removed using a vacuum suction line without coming in physical contact with the stained surface. The stained area is brushed twice lightly in opposite directions with a straight motion of a

dry absorbent tissue to remove any unabsorbed stain material.

The stains are rated against the white background of a clean blotter. Ratings of 1 through 5 are arrived at strictly on size (relative spread) of an individual stain while rating 6 through 10 determines relative wetting as measured by intensity of the stain against a standard.

In other words, a stain not even wetting the fabric could not change the color of the fabric and would have been completely removed from the surface thereof. The rating, therefore, would be 10. With increasing wetting of the area to which the stain has been applied there would be a greater color intensity therefore a lower rating until 6 is reached, whereupon, if the stain has migrated from its original boundary then one can assume complete wetting of the original area so that degree of migration becomes the determining factor. The greater the migration, the lower the number given. It will be appreciated that the test system is based on relative values, and yet provides unique reproducible valid results.

The three water borne stains are added together to give a possible maximum of 30. Likewise the oil borne stains are added to give a maximum possibility of 30. These may then be totalled for a maximum of 60.

To arrive at the launderability portion of the test, the stained fabrics are dried 24 hours. Laundering is then carried out by washing in an automatic washer with a quantity of a conventional detergent. The fabrics are then dried in an automatic dryer at the appropriate setting for the fabric type. They are then lightly dry ironed (stain side down) at the appropriate fabric setting.

The rating of launderability of stains is based on the same 1–10 system used for the static stain repellency tests. Again, it will be noted that the maximum rating after adding the results of the water borne stains will be 30, and similiarly 30 will be the total results regarding the oil borne stains. These two may be added together.

By rating both the initial static stain repellency and the launderability, a complete picture can be obtained not possible when only the initial stain reaction is determined.

COLGATE-PALMOLIVE TEST I

| | Initial static staining | | | | | |
|---|---|---|---|---|---|---|
| | Repellency | | | Launderability | | |
| Ex. | W.B.[1] | O.B.[2] | Total | W.B. | O.B. | Total |
| III | 19 | 18 | 37 | 26.5 | 20.5 | 46.5 |
| IV | 14.5 | 17 | 31.5 | 23.5 | 16 | 39.5 |
| V | 16 | 19 | 3.5 | 25.5 | 22 | 47.5 |
| VI | 15 | 19.5 | 34.5 | 23 | 22 | 45 |
| VII | 3 | 5 | 8 | 12 | 3 | 15 |
| VIII | 3 | 5 | 8 | 4 | 6 | 10 |

[1] Water borne stain.
[2] Oil borne stain.

As can be seen from a study of the above test results, the non-fluorinated polymer do not contribute a great deal of additional stain resistance. However, from the results set forth below they do, however, contribute ease of ironing not found in the unformulated starch and have ironing superiority even to starch-fluoropolymer combination.

| Examples | Aesthetic qualities, ease of ironing |
|---|---|
| III | Good. |
| IV | Very good. |
| V | Do. |
| VI | Fair. |
| VII | Poor. |

By carrying out replicates of the swatches treated by the formulations of Examples III to VII as before, but subjecting all of them to a single wash with a detergent in a conventional washing cycle followed by drying and ironing, durability results are obtained as follows:

COLGATE-PALMOLIVE TEST II

| | Durability (IW) static staining | | | | | |
|---|---|---|---|---|---|---|
| | Repellency | | | Launderability | | |
| Ex. | W.B. | O.B. | Total | W.B. | O.B. | Total |
| III | 4 | 7 | 11 | 6 | 6 | 12 |
| IV | 4 | 7 | 11 | 6 | 7 | 13 |
| V | 3 | 6 | 9 | 6 | 6 | 12 |
| VI | 3 | 6 | 9 | 6 | 6 | 12 |
| VII | 3 | 6 | 9 | 13 | 4 | 17 |

When one compares the results of Test II with Test I it will be noted that the stain repellency is almost completely eliminated and compares with the results of Example VIII or Test I.

## EXAMPLE IX

Example II is repeated wherein the propellant and amount thereof is varied as follows (with a corresponding change in percent water):

| | Percent |
|---|---|
| A. Isobutane | 5 |
| B. Isobutane | 10 |
| C. Isobutane | 20 |
| D. n-Butane | 8 |
| E. Freon 12 | 6 |
| F. Methyl chloride | 4 |
| G. Hexafluoroethane | 3 |
| H. Nitrous oxide | 6 |
| I. 4:1 mixture of isobutane and Freon 12 | 6 |

Excellent results are obtained.

## EXAMPLE X

Example I is repeated using the following water-soluble carbohydrates in the indicated amounts. Where more or less than 2.7% is used, there is a corresponding change in the water present:

| | Percent |
|---|---|
| A. Thin boiling wheat starch—fluidity 87 | 2.0 |
| B. Thin boiling wheat starch—fluidity 87 | 5.2 |
| C. Thin boiling wheat starch—fluidity 98 | 8.2 |
| D. Modified cornstarch—fluidity 60 | 3.1 |
| E. Modified cornstarch—fluidity 75 | 6.2 |
| F. Sulfated amylopectin (18 oz. starch) | 7.0 |
| G. Oxyethylated starch—fluidity 65 | 2.8 |

The results are comparable to Example I.

## EXAMPLE XI

Example I is against repeated except that the fluoro polymer amount is as follows:

A. 0.14%
B. 0.03%
C. 1.4%
D. 0.6%
E. 0.15%

The results are equivalent to those obtained in Example I.

As the above examples illustrate, the compositions of this invention produce excellent sizing along with unique water- and oil-repellency on textiles. The compositions may be applied to the textiles in any convenient manner although they are most superior when used in an aerosol form. Where the propellant in these compositions is more dense than the aqueous components, the package structure will, obviously, vary from those packages or container used with propellants which are less dense than and form an upper discrete liquid phase. Regardless of these variations, however, excellent properties are forthcoming in all instances.

Many substances may be added to the compositions of this invention, as pointed out above, and as will be obvious to one skilled in the art, the parameters are ex-

tremely varied, particularly in view of the fact that none of the additives need be soluble either in water or the selected propellant. Where it is desired, a compound may be added as a solution in a suitable solvent and such solution added to the aqueous compositions producing in most instances a dispersion of the said compound in the compositions. Many other variations will be apparent and it is clear that these may be resorted to without departing from the spirit and scope of this invention and that the specific embodiments set out herein are in no way limitative thereof.

What is claimed is:

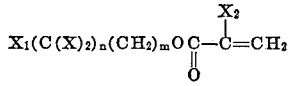
1. A containerized, non-durable, aqueous aerosol textile treating composition for sizing and rendering a textile oil and water repellent consisting of,

(A) a major amount of water-immiscible propellant mixture, and

(B) a minor amount of a component mixture of,

(1) a water soluble starch characterized by a fluidity value of 30 to 100, and

(2) a thermoplastic fluoro polymer of an alkyl acrylate containing 1–30 C in the alkyl group and at least 2.5 mole percent of a polymerizable compound of the formula



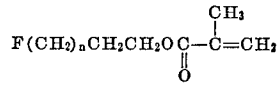
wherein X is selected from the group consisting of hydrogen, $C_1$ to $C_8$ alkyl, chlorine and fluorine: $X_1$ is selected from the group consisting of hydrogen, chlorine and fluorine, and $X_2$ is selected from the group consisting of hydrogen, $C_1$ to $C_4$ alkyl and halogen: *n* has a value of 3 to 30: *m* has a value of 1 to 3; and at least 70%, but at least 6 of the X's are fluorine and said thermoplastic fluoro polymer having a molecular weight of less than 30,000, said components (1) and (2) being present in the range of 1:2 to 100:1.

2. A composition as defined in claim 1 wherein the polymer contains from 1 to 75 mole percent of a $C_1$ to $C_{30}$ alkyl acrylate in polymerized form.

3. A composition as defined in claim 2 wherein the polymer contains from 1 to 10 mole percent of a $C_2$ to $C_4$ alkyl acrylate.

4. A composition as defined in claim 3 wherein the polymer contains from 1 to 10 mole percent N-methylol acrylamide.

5. A composition as defined in claim 4 wherein the formula of the polymerizable compound (B)(2) is



6. A composition as defined in claim 1 wherein the starch is acetylated amylopectin.

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