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FABRIC TREATING COMPOSITION AND PROCESS

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The present invention relates to a novel fabric treating composition and process. More particularly the present invention relates to novel urethane emulsion systems for use in imparting crease and, notably, abrasion resistant properties to fabrics, particularly cotton goods.

An object of the present invention is to provide novel urethane emulsion systems and a process for the use thereof whereby improved crease and abrasion resistant properties may be readily imparted to fabrics without deleteriously affecting the fabrics.

Another object of the present invention is to provide urethane emulsion systems which may be readily cured at operating temperatures feasible for use with fabric materials.

A further object of the present invention is to provide nonflammable, urethane containing compositions which may readily be used in conventional fabric finishing equipment to impart improved wear and abrasion resistant properties to the fabrics treated therewith.

A still further object of the present invention is to provide one-package urethane emulsion systems which are stable when stored for protracted periods of time.

The textile industry has long sought textile finishing compositions which may be readily used in existing textile finishing equipment for imparting improved wear, crease and abrasion resistant properties to various types of fabrics. The industry has particularly sought such textile finishing compositions for use on cotton goods of the denim and wash and wear types which are more apt to be subjected in the course of normal usage to rough and/or repeated wear and laundering than other types of fabrics. A number of textile finishing compositions which have been suggested for these purposes, however, have proven to be unsuitable for practical use because of the fact that they could not be very readily and/or safely processed with the fabric being treated and/or in the equipment available for use. Some have required operating temperatures that would be deleterious to the fabric, others have required their use in expensive and/or flammable solvent systems and the slight improvement in abrasion resistant properties actually imparted to the fabric by other of these compositions has not been of sufficient magnitude to warrant the expense of the additional processing step and compositions used therein.

It has now been unexpectedly found, according to the present invention, that greatly improved wear and, in particular, resistance to abrasion properties can be readily and safely imparted to fabric materials using conventional fabric finishing equipment if a novel oil-in-water emulsion system containing at least one blocked, curable, urethane prepolymer is applied to the fabric being treated and the treated fabric is then subjected to moderate heat to evaporate solvent and water from the emulsion system and unblock the blocked prepolymer so as to permit the unblocked prepolymer to be cured.

The fabric is so treated with the emulsion systems of the present invention as to insure that the cured prepolymers impart to the fabric a dry, solids pickup of about 0.5 to 15% based on the weight of the fabric. By "dry, solids pickup" is meant, within the concept of the present invention, the weight percent of the cured prepolymers together with other solids such as may be bound within the polymer matrix, e.g., pigments, residues

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of emulsifying agents, colloid stabilizers, curing catalysts, etc.

The novel oil-in-water emulsion systems of the present invention are prepared by first producing a solution of at least one blocked, curable, urethane prepolymer in an organic solvent which also contains a curing agent and then emulsifying the prepolymer solution in water to attain an oil-in-water emulsion. By oil it is meant, within the concept of the present invention, the solution of the blocked urethane prepolymer and the curing agent in the organic solvent. For reasons of economy and technical feasibility it is preferable to prepare prepolymer solutions which have as high a solids content as possible. By "solids content" is meant the weight percent of non-solvent and non-aqueous materials present in the liquid systems of this invention such as the total weight percent of prepolymers, blocking agents, emulsifying agents, colloid stabilizers, curing agents, fillers, etc. as would be present in the emulsions, or, in the case of prepolymer solutions, the weight percent of prepolymers, blocking agents and curing agents present in the solvent. Solutions which contain about 30% solids may be used. However, it is preferable for reasons of transportation economy to prepare solutions which contain at least about 50% solids. For similar reasons when the emulsion is to be transported it should be prepared so as to have a solids content of as high as possible. When the emulsion is to be used it may be diluted down to a solids content of the order of 1-15%. The low solid content emulsions may be formed directly from a solution or a higher solids content emulsion.

In preparing the prepolymer solutions the prepolymer, solvent and blocking agent are preferably added to the mixing chamber, in that order, and mixed together. Since the reaction of the blocking agent with the prepolymer will usually cause an exotherm, it is preferable to allow the resulting solution to cool down to about room temperature before admixing the cure agent therewith. The prepolymer solution containing the blocked prepolymer and the curing agent can be stored with or without adjuvants such as surface active agents, colloid stabilizers, cure catalysts and/or pigments without interfering with the stability of the system. The adjuvants may also be added concurrently with or subsequent to the emulsification of the prepolymer solution.

In preparing the emulsions, particularly where the prepolymer solution has been stored for some time, it is advantageous to use warm water, i.e., about 100° F. To prepare the most stable emulsions the water should be mixed relatively slowly with the prepolymer solution until the inversion point is reached and then the remainder of the water can be added at a faster rate. The phase change from water-in-oil to oil-in-water can be observed by noting a decrease in viscosity or a change in the electrical conductivity of the emulsion. Another simple test for determining the type of emulsion is the dilution test, i.e., if the emulsion is readily dilutable with water it is an oil-in-water emulsion, if not, it is a water-in-oil emulsion.

The urethane prepolymers which may be used in the novel compositions of the present invention may have an ester and/or ether backbone. The ester type materials are preferred. The most preferred of these ester materials is castor oil and esters prepared from ethylene glycol/propylene glycol/adipic acid ester reaction products. The prepolymers are formed by so reacting the ester and/or ether raw materials and one or more diisocyanate group containing materials such as toluene diisocyanate, diphenylmethane diisocyanate, 1,5-naphthalene diisocyanate and hexamethylene diisocyanate that the resulting prepolymer has an active —NCO content of about 2.5 to 30%.

The prepolymers may be blocked with one or more of any of the known urethane prepolymer blocking agents including ketoximes, such as methyl ethyl ketoxime, cyclohexanone oxime, and methyl methyl ketoxime; imines such as ethylene imine and propylene imine; alcohols such as methanol, ethanol and propanol and secondary amines such as diethyl amine, morpholine and dibutyl amine. The ketoxime blocked prepolymers are preferable because they generally have better cure temperature properties and can be stored rather indefinitely. The most preferred blocking agent is methyl ethyl ketoxime. Imine blocked prepolymers may be used where the emulsion system is to be used relatively soon after it is manufactured and alcohol and secondary amine blocked prepolymers may be used where higher cure temperatures can be tolerated. In blocking the prepolymers the prepolymer and blocking agent are reacted in a mol ratio of active —NCO/blocking agent which has a range of about 1/1 to 2/1. It is preferable to use stoichiometrically reactive quantities. Although the prepolymer and the blocking agent may be prereacted before the blocked system is put into solution it is preferable to react the two materials in the organic solvent to avoid processing problems that may otherwise arise.

The organic solvents which may be used to prepare the urethane prepolymer solutions include Cellosolve acetate, aromatic hydrocarbon solvents such as benzene, toluene and xylene; chlorinated hydrocarbon solvents such as methylene chloride, trichloroethylene and perchloroethylene, and ketones such as acetone and methyl ethyl ketone. The use of alcohols as the organic solvent should be avoided because of the tendency of the alcohol to interfere with the blocking reaction where the blocking reaction takes place in the solvent. The solvents may be used alone or in combination with one another.

In preparing the emulsion it is necessary to use emulsifying agents to prepare emulsions that will be stable for long periods of time. Where the emulsion is to be used within a relatively short time after it is made little or no emulsifying agent is needed. Various amounts of one or more different types of emulsifying agents can be used alone or in combination with one another to obtain a stable emulsion. The emulsions may be stabilized by the use therein of about 0.5 to 5 parts by weight per 100 parts by weight of the emulsion system of one or more surface active agents such as sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan tristearate, sorbitan trioleate, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, or other common surface active agents.

The stability of the emulsion system may also be enhanced by the incorporation therein of 0.25 to 1 part by weight of at least one colloid stabilizer per 100 parts by weight of the emulsion system. Colloid stabilizers which may be used for this purpose include silicon dioxide, carboxymethyl cellulose, polymethacrylates, hydroxy ethyl cellulose and methyl cellulose. Hydroxy ethyl cellulose is the preferred stabilizer since the emulsions produced therewith tend to have longer shelf life. Where the emulsion is to be used relatively soon after it is made other stabilizers may be used.

As noted above the prepolymer is unblocked during the heating step in which the solvent and water values are also removed from the emulsion. The prepolymer is then cured during this heating operation after it is unblocked by a curing agent which is also incorporated into the emulsion system for this purpose. The curing agent is used in such quantities as to insure that there is available in the emulsion system for the cure reaction an active —NCO/active hydrogen ratio which has a range of about 0.5/1 to 2/1. The active hydrogen may be in the form of OH, NH₂ or SH. For emulsion stability purposes it is preferable to use OH containing cure agents as the source of the active hydrogen. Cure agents which may be used for this purpose include N,N,N',N'-tetrakis

(2-hydroxypropyl) ethylene diamine, triisopropanolamine and triethanolamine. The cure agents may be used alone or in combination with one another. N,N,N',N'-tetrakis-(2-hydroxypropyl) ethylene diamine and triethanolamine are the preferred curing agents because they tend to have both faster cure cycles and better stability properties in the solvent and/or emulsion system. Because the temperatures needed to cause the unblocking reaction, according to the present invention, are in the order of about 180 to 300° F. most of the water present in the emulsion system will be evaporated off before the unblocking reaction occurs and, therefore, only a relatively small amount of water will be present during the cure reaction between the unblocked prepolymer and the curing agent. Since water also contains reactive hydrogen in the form of OH which will react with the active —NCO groups some, if not all, of the water remaining during the curing reaction, however, will react with and cure some of the unblocked prepolymer. It has been found that the amounts of water that will react with the prepolymer under these conditions is not such as to cause any deleterious effects upon the desired properties of the cured system. Ordinary tap water may be used as the source of water for forming the emulsions of the present invention. For emulsion stability purposes, however, it is preferable to use distilled or deionized water.

Where needed to speed up the cure cycle about 0.1 to 0.5 part by weight of one or more catalysts per hundred parts by weight of the emulsion system may be used. Catalysts such as lead octoate, lead acetyl acetonate, triethylene diamine, lead 2-ethylhexoate, lead benzoate, lead oleate and stannous octoate may be used for this purpose. Without the catalysts the unblocked prepolymers will cure according to the process of the present invention in about 10 to 30 minutes at 180–300° F. With the catalysts, particularly lead octoate, the prepolymers will cure in about 5 to 15 minutes at 180 to 300° F. The inclusion of the catalysts in the emulsion system will not interfere with the stability of the emulsions upon storage at ambient temperatures.

One or more pigments such as titanium dioxide, carbon black, iron oxide and silica may also be incorporated into the emulsion systems of the present invention to impart improved color properties to the fabrics treated therewith.

The textile finishing compositions of the present invention may be used to treat fabrics in various forms such as denims, gabardines, khakis, industrial garb, non-woven fabrics, drills, twills, jeans, tickings, tape and bindings. For the treatment of non-woven fabrics, in particular, the art has long sought such compositions of the present invention wherewith improved binding, abrasion resistance, hand and crease resistance properties, may be readily and safely imparted to the fabrics without substantially stiffening the fabric.

The following examples are merely illustrative of the present invention and are not intended as a limitation upon the scope thereof.

EXAMPLE 1

Preparation of a prepolymer

297.6 g. (4.8 moles) of ethylene glycol, and 91.2 g. (1.2 moles) of propylene glycol were charged to a glass reaction vessel fitted with agitator, thermometer, nitrogen inlet tube, steam jacketed condenser, cold water condenser for refluxing the water produced during the reaction. To the reaction system there was then added 800 g. of adipic acid (5.5 moles) to provide for an insufficiency of acidic groups, and thus insure that the resultant copolyester molecules were hydroxy-terminated.

This mixture was heated to 160° C., and as esterification proceeded with nitrogen purging and stirring, the water resulting from the esterification reaction was refluxed until the temperature of the reaction system fell to 130° C., which took about 2 hours, and then the water was removed by distillation from the reaction vessel. As

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the water was removed from the system, the reaction temperature was allowed to rise to 200° C., until most of the theoretical quantity of water from the esterification reaction had been removed, about 97%. The heating was continued until an acid number of less than 3 was obtained. The reaction was then stopped by cooling the pot to ambient temperature.

361.13 g. (0.25 equivalent weight) of the copolyester glycol produced above were charged to a glass reactor fitted with agitator, thermometer, feed funnel and cold water reflux condenser which was open to the atmosphere through a drying tube. The pot temperature (temperature of the reaction system) was raised to 50° C., and 47.0 g. (0.54 eq. wt.) of an 80/20 isomer mixture of 2,4/2,6-toluene diisocyanate was added within a 10 minute interval. The reaction proceeded under a blanket of nitrogen at 80° C. for four hours. The isocyanate-terminated product had about 3% by weight of reactive isocyanate by analysis and an equivalent weight of approximately 1400.

EXAMPLE 2

Preparation of a urethane prepolymer

A glass lined reactor was charged with 77 ml. of toluene diisocyanate and heated to a temperature of 85° F. Castor oil was fed into the reactor slowly over a 70 minute period in an amount such that the mixture in the reactor contained about 2.5 isocyanate groups to each hydroxyl group present in the polyhydric castor oil. During this addition, the temperature of the reactor was permitted to increase to about 130° F. and after addition was completed, the reactor was heated to 185° F. over a period of 30 minutes. It was then kept at this temperature for an additional hour. The contents of the reactor were then cooled as rapidly as possible to 100° F. A liquid urethane prepolymer having an active isocyanate analysis between about 10.4 percent and 10.8 percent resulted.

EXAMPLE 3

Preparation of an emulsion with a catalyst to be used to impart crease and abrasion resistant properties to fabrics according to the present invention

1000 parts by weight of a prepolymer having an active —NCO content of 10.6% and prepared as in Example 2 were thoroughly mixed with 340 parts by weight of toluene. 192 parts by weight of methyl ethyl ketoxime were added to the prepolymer/toluene mixture in small increments with constant stirring while simultaneously cooling the system to keep the temperature of it under 130° F. The mol ratio of active —NCO to blocking agent was 1.15/1. The system was then allowed to stand for about 1½ hours at room temperature. 161 parts by weight of N,N,N',N'-tetrakis(2-hydroxypropyl) ethylene diamine were then added to the resulting solution and stirred in well. The mol ratio of —NCO to active hydrogen was 1.15/1. The resulting solution had a solids content of about 80%.

To 1000 parts by weight of the 80% solids solution prepared above which had been heated to about 100° F. there was successively added with stirring 20 parts by weight of a 30/70 (by weight) mixture of sorbitan monolaurate and polyoxyethylene sorbitan monolaurate and 8 parts by weight of lead octoate. Tap water, heated to about 100° F., was then slowly added to the resulting mixture with constant stirring until the resulting emulsion changed from a water-in-oil to an oil-in-water emulsion and more water was then added at a faster rate until a total of 980 parts by weight of water had been mixed into the system. The mixing was continued until a uniform emulsion was obtained. The resulting emulsion was a stable, one package system having a solids content of about 40%.

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A second emulsion was also prepared as above using 7.5 parts by weight of a 50/50 (by weight) mixture of lead octoate and triethylene diamine as the catalyst.

EXAMPLE 4

Preparation of an emulsion without a catalyst to be used to impart crease and abrasion resistant properties to fabrics according to the present invention

580 parts by weight of toluene, 1000 parts by weight of a prepolymer prepared as in Example 2 and having an active —NCO content of 10.65%, 192 parts by weight of methyl ethyl ketoxime and 161 parts by weight of N,N,N',N'-tetrakis(2-hydroxypropyl) ethylene diamine were mixed together as described in Example 3 to form a prepolymer solution having a solids content of about 70%. The mol ratio of active —NCO to both the blocking agent and the active hydrogen of the curing agent was 1.15/1.

1000 parts by weight of the above prepared prepolymer solution, 15.8 parts by weight of a 30/70 (by weight) mixture of sorbitan monolaurate and polyoxyethylene sorbitan monolaurate and 980 parts by weight of tap water were used as described in Example 3 to form a stable emulsion having a solids content of about 35%.

EXAMPLE 5

Preparation of an emulsion to be used to impart crease and abrasion resistant properties to fabrics according to the present invention

1000 parts by weight of a prepolymer prepared as in Example 1 and having an active —NCO content of 3.17%, 450 parts by weight of toluene, 57 parts by weight of methyl ethyl ketoxime and 48 parts by weight of N,N,N',N'-tetrakis(2-hydroxypropyl) ethylene diamine were mixed together as in Example 3 to produce a prepolymer solution having a solids content of about 70%. The mol ratio of active —NCO to both the blocking agent and the active hydrogen of the curing agent was 1.15/1.

1000 parts by weight of the prepolymer solution prepared above were then emulsified with 10 parts by weight of a 10/90 (by weight) mixture of sorbitan monolaurate and polyoxyethylene sorbitan monolaurate, 7 parts by weight of lead octoate, 5 parts by weight of Natrosol 250-H (hydroxy ethyl cellulose sold by Hercules Powder Company) and 990 parts by weight of tap water as described in Example 3. The resulting emulsion was a stable one package system which had a solids content of about 35%.

The emulsion may also be made and used effectively without a catalyst.

EXAMPLE 6

Preparation of emulsions to be used to impart crease and abrasion resistant properties to fabrics according to the present invention

100 parts by weight of a prepolymer having an active —NCO content of 3.17% and prepared as in Example 1, 470 parts by weight of toluene, 57 parts by weight of methyl ethyl ketoxime and 48 parts by weight of N,N,N',N'-tetrakis(2-hydroxypropyl) ethylene diamine were mixed together as in Example 3 to form a prepolymer solution having a solids content of about 70%. The mol ratio of active —NCO to both the blocking agent and the active hydrogen of the curing agent was 1.15/1.

1575 parts by weight of prepolymer solution prepared above 158 parts by weight of a 10/90 (by weight) mixture of sorbitan monolaurate and polyoxyethylene sorbitan monolaurate, 126 parts by weight of Cab-O-Sil (colloidal silica sold by Godfrey L. Cabot, Inc.), and 1415 parts by weight of tap water, were emulsified as in Example 3 to produce a stable emulsion having a solids content of about 35%.

A second stable emulsion was prepared as above using xylene instead of toluene as the solvent. Methylene chloride or perchloroethylene may also be used as the solvent to produce other such stable emulsions.

EXAMPLE 7

Preparation of an emulsion to be used to impart crease and abrasion resistant properties to fabrics according to the present invention

1000 parts by weight of prepolymer having an active —NCO content of 3.17% and prepared as in Example 1, 475 parts by weight of trichloroethylene, 57 parts by weight of methyl ethyl ketoxime and 48 parts by weight of N,N,N',N'-tetrakis(2-hydroxypropyl) ethylene diamine

Sample	Tensile strength		Tear strength		Hand	Crease recovery		Abrasion resistance
	Warp	Filling	Warp	Filling		Initial	Final	
Control.....	53.9	52.1	86.2	74.8	12.5	120	146	340
Cured 5 minutes.....	54.3	54.6	77.1	75.4	22.0	117	160.8	1,187.5
Cured 15 minutes.....	54.3	55.5	77.3	76.6	28.1	115.8	187.6	1,705
Cured 30 minutes.....	56.8	53.0	77.8	75.1	26.4	151.4	189.2	1,731

were mixed together as in Example 3 to form a prepolymer solution having a solids content of about 70%. The ratio of active —NCO to both blocking agent and the active hydrogen of the curing agent was 1.15/1.

1000 parts by weight of the prepolymer solution prepared above, 158 parts by weight of 1.6/14/2 (by weight) blend of sorbitan monolaurate and polyoxyethylene sorbitan monolaurate, 2.2 parts by weight of Cab-O-Sil and 1420 parts by weight of tap water were emulsified as in Example 3 to produce a stable emulsion having a solids content of about 35%.

EXAMPLE 8

Preparation of an emulsion to be used to impart crease and abrasion resistant as well as improved color properties to fabrics according to the present invention

600 parts by weight of a prepolymer solution having a solids content of about 70% and prepared as in Example 7 from a prepolymer having an active —NCO content of 3.21% and prepared as in Example 1 was emulsified with 6 parts by weight of a 10/90 (by weight) mixture of sorbitan monolaurate and polyoxyethylene sorbitan monolaurate, 3 parts by weight of hydroxy ethyl cellulose, 120 parts by weight of Titanox-A-WD (titanium oxide sold by National Lead Company) and 594 parts by weight of tap water. The hydroxy ethyl cellulose and the blend of surface active agents was first mixed with the prepolymer solution. The water and the titanium dioxide were mixed together in a Waring Blendor and then mixed with the rest of the formulation to make a stable emulsion.

EXAMPLE 9

Treatment of fabric with urethane emulsions

A quantity of the urethane emulsion prepared as in Example 4 was diluted with tap water in a ratio of two parts of water to one part of emulsion. The diluted emulsion which now had a solids content of about 11.7% was then padded on scoured and bleached cotton print cloth to a wet pickup of 100% with a laboratory size three roll padder. The padded fabric was then dried for 10 minutes at 180° F. A sample of the same type cloth was padded with tap water and dried for 10 minutes at 180° F. to serve as a control sample. The fabric padded with the emulsion was cut into 12 inch square samples. One set of samples was cured at 300° F. for 15 minutes, one set was cured at 300° F. for 5 minutes and one set at 300° F. for 30 minutes.

The padded and cured samples and the control sample were then tested for tear and tensile strength, crease recovery, hand and abrasion resistance. Tear strength was measured on the Elmendorf tear tester, tensile strength was measured on the Scott pendulum tester using the grab method, hand was measured on the Handle-O-Meter, crease recovery on the Monsanto crease recovery tester which was used to measure the angle recovery body immediately on placing the sample in the tester and after a five minute interval and abrasion resistance was measured on the Tabor abrader. The results obtained from these tests are shown in the following table. Tensile strength is reported in lbs. per square inch, tear strength is reported in Elmendorf units, crease recovery is indicated in terms

of total crease angle (warp and filling) and abrasion resistance is reported in cycles to first appreciable wear. These results indicate that the novel urethane emulsions of the present invention can be efficiently and safely used to treat fabric materials in existing fabric treating equipment without adversely affecting the tensile or tear strength of the fabric. The slight reduction in tear strength in the samples treated with the urethane emulsions is due to the attendant stiffening effect. The hand of the treated fabric is stiffened. The results also disclose a moderate improvement in crease recovery and a substantial improvement in abrasion resistance in the treated fabric.

EXAMPLE 10

Treatment of fabric with urethane emulsions

Three pieces of cotton textile fabric were each subjected to a different treatment as follows.

Fabric #1 was padded, at 70° wet pickup, with a bath containing:

- (a) 28.8% by weight of urea-formaldehyde resin monomers (Rhonite R-1, Rhom & Hass)
- (b) 0.5% by weight of a catalyst H-7 (zinc complex sold by Rohm & Haas)
- (c) 0.5% by weight of a wetting agent, isooctyl phenyl polyethoxy ethanol
- (d) Balance deionized water

Fabric #2 was padded, 70% wet pickup with a bath containing:

- (a) 28.8% by weight of urethane emulsion produced as in Example 4
- (b) 0.5% by weight of isooctyl phenyl polyethoxy ethanol
- (c) Balance deionized water

Fabric #3 was padded, at 70% wet pickup, with a bath of deionized water containing 0.5% by weight of isooctyl phenyl polyethoxy ethanol. The padding treatment gave an approximate solids pickup on fabrics 1 and 2 of 20%. The three fabrics were then dried at 180° F. for 30 minutes and fabrics 1 and 2 were cured at 300° F. for 5 minutes, washed in water at 140° F. with soap, rinsed and dried at 180° F. for 50 minutes and ironed smooth. The three fabrics were each cut in half and one half of each fabric was tested after being conditioned at 70° F. and 65% relative humidity for 24 hours and the other half of each fabric was tested after being subjected to accelerated ageing (closed contained method, CCC-T-

191b, method 5851) and conditioned. The following tests were then conducted on each half of each fabric:

- (1) Tensile strength (Ravel Strip Method, CCC-T-191b, method 5104)
- (2) Tear strength (Falling Pendulum Method, CCC-T-191b, method 5132)
- (3) Abrasion resistance (Tabor Method, CCC-T-191b, method 5306)
- (4) Crease recovery; dry (Monsanto Method, CCC-T-191b, method 5212)
- (5) Crease recovery; wet (Monsanto Method, CCC-T-191b, method 5212 except that test was conducted under water)

Test results

TENSILE STRENGTH (POUNDS FORCE TO BREAK 1 INCH STRIP)—AS TREATED

	Control fabric		Urea-formaldehyde		Urethane emulsion	
	Warp	Filling	Warp	Filling	Warp	Filling
High...	61.0	61.0	35.0	33.0	60.0	61.0
Low...	51.0	34.0	25.0	23.0	52.0	45.0
Ave...	56.8	48.6	30.3	28.7	55.8	53.4

AS AGED

High...			87	90	123	125
Low...			85	85	108	105
Ave...	150	150	86.2	86.0	116.8	115.3

ABRASION RESISTANCE CYCLES—AS TREATED

	First wear	Des. wear	First wear	Des.	Urethane emulsion	
					First wear	Des.
High...	350	625	175	400	575	875
Low...	135	350	100	300	300	700
Ave...	252	545	125	353	380	785

AS AGED

High...	260	820	225	655	700	1,747
Low...	250	800	130	570	440	1,190
Ave...	255	810	1,175	6,125	555	1,427

CREASE RECOVERY (RECOVERY ANGLE WARP AND FILLING)—AS TREATED DRY

	Control		Urea-formaldehyde		Urethane emulsion	
	Initial	Final	Initial	Final	Initial	Final
High...	110	142.5	220	232.5	130	175
Low...	97.5	130	172.5	187.5	102.5	150
Ave...	106	135.5	180	200.5	112.9	156.8

AS TREATED WET

High...			185	207.5	1,725	230
Low...			160	190	140	2,025
Ave...	106	135.5	1,725	200	1,615	2,165

AS AGED DRY

High...	132.5	162.5	177.5	217.5	115.0	80
Low...	100	127.5	152.5	185	94	150
Ave...	115	142	165	195.5	109.5	165.5

AS AGED WET

High...	135	147.5	185	205	167.5	222.5
Low...	95	105	150	177.5	140	195
Ave...	116	127.5	164.5	189.5	152.5	207

- 15 The test results show that the urethane emulsions impart much better abrasion resistance properties to fabrics treated therewith, after washing, than imparted by the Urea-Formaldehyde materials which are conventional fabric treating materials. Both types of materials imparted comparable tensile strength and stiffness properties to the fabrics treated therewith.

EXAMPLE 11

- 20 *Comparative evaluation of fabrics treated with urethane emulsions according to the present invention and fabrics treated with butadiene/acrylonitrile copolymers*

- 25 Pieces of a 10 ounce g./square yard blue denim were desized in enzyme (amolytic) dried and padded at 70% wet pickup with urethane emulsions prepared in Examples 3 and 5 and butadiene/acrylonitrile (without catalysts or colloid stabilizer) copolymer latexes (Hycar 1512 and Hycar 1572 sold by Goodrich Chemical Company) to give dry solids pickups of approximately 1%, 5% and 10% for each of the four polymer systems being evaluated. The padded fabrics were then dried at 150° F. for 30 minutes and cured at 300° F. for five minutes. The baths used had the following compositions.

- 40 1% Hycar #1512: Percent
Latex (45% solids) ----- 3.1
Distilled water (by weight) ----- 96.9
- 1% Hycar #1572:
Latex (50% solids) ----- 2.8
Distilled water (by weight) ----- 97.2
- 45 1% urethane emulsion (made as in Example 3):
Emulsion ----- 3.5
Distilled water (by volume) ----- 97.5
- 1% urethane emulsion (made as in Example 5):
Emulsion ----- 3.5
Distilled water (by volume) ----- 97.5
- 50 5% Hycar #1512:
Latex (45% solids) ----- 15.5
Distilled water (by weight) ----- 84.5
- 55 5% Hycar #1572:
Latex (50% solids) ----- 14.0
Distilled water (by weight) ----- 86.0
- 5% urethane emulsion (made as in Example 3):
Emulsion ----- 16.5
Distilled water (by volume) ----- 83.5
- 60 5% urethane emulsion (made as in Example 5):
Emulsion ----- 16.5
Distilled water (by volume) ----- 83.5
- 10% Hycar #1512:
Latex (45% solids) ----- 31.0
Distilled water (by weight) ----- 69
- 65 10% Hycar #1572:
Latex (50% solids) ----- 28
Distilled water (by weight) ----- 72
- 70 10% urethane emulsion (made as in Example 3):
Emulsion ----- 33
Distilled water (by volume) ----- 67
- 10% urethane emulsion (made as in Example 5):
Emulsion ----- 33
Distilled water (by volume) ----- 67
- 75

The treated fabrics were then subjected to tests for abrasion resistance, tensile strength and stiffness both before and after the equivalent of ten commercial launderings. Fabric samples treated with each of the baths were divided into two groups and one group of samples were subjected to a 45 minute washing treatment at 210° F. with soap followed by two 15 minute rinses at 180° F. This test procedure is equal to 10 commercial launderings without bleach. The other group of samples were not subjected to the washing treatment. Both groups of samples were further conditioned at 70° F. and 65% relative humidity for 24 hours and subjected to the following tests:

Abrasion resistance—Wyzenbeek, Method CCC-T-191b, #5304 (abrading to total destruction)
Tensile—Ravel Strip, Method CCC-T-191b, #5104.1
Stiffness—Cantilever, Method CCC-T-191b, #5202

before and after an accelerated laundering without bleach as in Example 11. The results are as follows:

5	Abrasion resistance—warp and filling cycles to total destruction	Urethane emulsion of—			
		35% solids produced as in Example 5		15% solids produced as in Example 3	
10	Unlaundered sample.....	2,614		1,582	
	Laundered sample.....	2,146		1,658	
15	Tensile strength (lbs.)	Warp	Filling	Warp	Filling
15	Unlaundered sample.....	136.0	61.6	129.2	72.1
	Laundered sample.....	127.0	54.7	129.7	60.4
15	Stiffness (inches, overhang)				
	Unlaundered sample.....	2.53	2.22	4.95	3.84
	Laundered sample.....	2.32	2.00	4.00	2.58

ABRASION—AVERAGE WARP AND FILLING (WYZENBEEK)—CYCLES TO TOTAL DESTRUCTION

	As applied			As washed		
	1%	5%	10%	1%	5%	10%
Hycar #1512.....	1,621	813	2,090	417	549	834
Hycar #1572.....	530	622	986	445	731	1,277
Urethane emulsion prepared as in Example 5.....	545	754	1,255	912	1,026	1,764
Urethane emulsion prepared as in Example 3.....	466	701	935	609	729	1,524
Original.....			(472)			(309)

TENSILE STRENGTH—LBS. TO BREAK

	As applied						As washed					
	1%		5%		10%		1%		5%		10%	
	W	F	W	F	W	F	W	F	W	F	W	F
Hycar #1512.....	94.7	51.6	108.4	57.6	110.5	61.5	96.4	52.9	95.5	56.1	99.5	51.9
Hycar #1572.....	112.7	55.4	127.2	56.4	132.8	60.5	106.8	49.6	111.8	57.1	120.2	56.3
Urethane emulsion prepared as in Example 3.....	113.7	53.4	125.4	59.3	117.9	59.7	107.2	54.6	112.3	51.7	110.7	56.3
Urethane emulsion prepared as in Example 5.....	119.0	53.3	112.8	49.5	122.4	56.3	117.0	50.6	101.5	40.1	119.3	54.6

W=Warp. F=Filling.

STIFFNESS—INCHES OVERHAND OF 1" WIDE SAMPLE—AVERAGE WARP AND FILLING TO GIVE BEND OF 53°

Hycar #1512.....	2.17	2.75	2.80	1.97	2.42	2.40
Hycar #1572.....	1.47	2.50	2.30	1.47	1.95	2.02
Urethane emulsion prepared as in Example 3.....	2.25	2.35	2.25	2.17	2.32	2.60
Urethane emulsion prepared as in Example 5.....	2.15	2.35	2.50	2.10	2.10	2.50
Original unsized.....			1.80			1.80
Average size.....			3.07			2.07

EXAMPLE 12

Evaluation of fabrics treated with urethane emulsions containing a cure catalyst

Pieces of a 10 ounce/square yard blue cotton denim material were desired, dried and padded as in Example 11 to give a 70% wet pickup and a 10% dry solids pickup with urethane emulsions prepared as in Examples 3 and 5 (with a catalyst and without a colloid stabilizer). The padding bath compositions used are—

Bath #1: 500 g. of a urethane emulsion prepared as in Example 5 (35% solids) 1000 g. water

Bath #2: 1000 g. of a urethane emulsion prepared as in Example 3 with a solids content of 15%

The fabric thus treated were then dried, cured and tested

These results illustrate that the use of a urethane cure catalyst with the urethane emulsions of the present invention aids in further improving the abrasion resistance properties of the fabrics treated therewith.

We claim:

1. An oil-in-water emulsion comprising

(A) an oil phase comprising

(1) an inert organic solvent,

(2) a blocked urethane prepolymer dissolved in said solvent and having an isocyanate content as present in the prepolymer prior to blocking from about 2.5 percent to 30 percent by weight and further having a ratio of isocyanate groups as present in the prepolymer prior to blocking to active hydrogen groups as present in the blocking agent prior to blocking which is in the range of about 1/1 to about 2/1,

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- (3) a curing agent for said urethane prepolymer dissolved in said solvent and being present in such quantity so as to provide a ratio of isocyanate groups as present in the prepolymer prior to blocking to active hydrogen groups as present in the curing agent which is in the range of about 0.5/1 to 2/1, said active hydrogen groups being selected from the class consisting of OH, NH₂ and SH groups;
- (B) an aqueous phase in which said oil phase is dispersed; and
- (C) at least one organic emulsifying agent in contact with said oil and aqueous phases and being present in quantities of about 0.5 to 5 parts by weight per one hundred parts by weight of said emulsion.
2. An oil-in-water emulsion as in claim 1 wherein said inert organic solvent is selected from the class of organic solvents consisting of ketones ester solvents, aromatic hydrocarbon solvents and chlorinated hydrocarbon solvents.
3. An oil-in-water emulsion as in claim 1 wherein said blocked urethane prepolymer is formed as the reaction product of (a) a blocking agent selected from the class of blocking agents consisting of aliphatic ketoximes, aliphatic imines, primary alcohols and secondary amines, and (b) urethane prepolymers selected from the group consisting of ester and ether based prepolymers.
4. An oil-in-water emulsion as in claim 1 further comprising at least one curing catalyst dissolved therein, said curing catalyst being selected from the group of curing catalysts consisting of lead octoate, lead acetyl acetate, triethylene diamine, lead 2-ethyl hexoate, lead benzoate, lead oleate and stannous octoate.

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5. An oil-in-water emulsion as in claim 1 further comprising at least one colloid stabilizer in contact with said oil and water phases and being present in quantities of 0.25 to 1 part by weight per one hundred parts by weight of said emulsion.
6. A process for imparting improved abrasion resistant properties to fabrics comprising
- (A) treating said fabric with the oil-in-water emulsion of claim 1;
- (B) heating the thus treated fabric to temperatures of 180 to 300° F. to at least substantially remove solvent and water values therefrom and promote the unblocking and cure of said urethane prepolymer, and
- (C) cooling and recovering an abrasion resistant fabric.
7. A process as in claim 6 wherein said fabric is treated with said oil-in-water emulsion so as to impart to said fabric at least 0.5 percent by weight of said urethane prepolymer based on the weight of said fabric.
8. The abrasion resistant fabric product obtained by the process of claim 6.

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