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ETHYL CELLULOSE-COATED TEXTILE FABRIC

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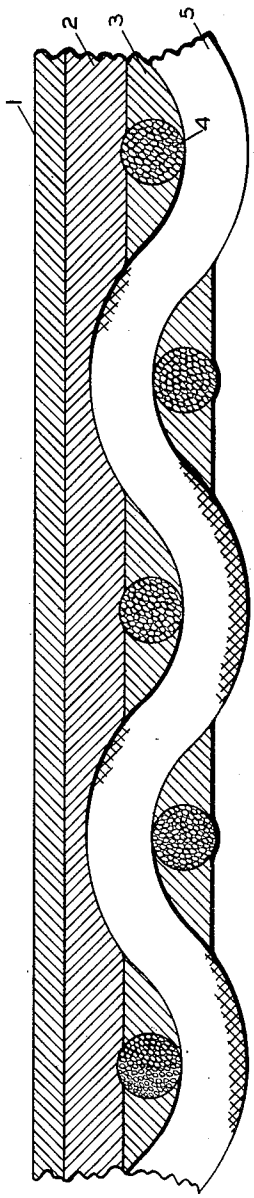

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ETHYL CELLULOSE-COATED TEXTILE FABRIC

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9 Claims. (Cl. 117—86)

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This invention relates to improved textile coatings and more particularly to textiles coated with cellulose ethers, said coated textiles being capable of retaining their flexibility at low temperatures and of retaining their plasticizers without blocking at high temperatures.

It is generally known that lacquers containing a film-forming polymer, whether plasticized or unplasticized, will stiffen textile fabrics when the lacquer penetrates the cloth, unless the proportion of film former in the lacquer is very low or unless the amount of solids applied to the cloth is likewise low. On the other hand, textile fabrics wetted with a high boiling liquid, such as an oil or other type of plasticizer, possesses a pleasing drape and handle free of papery stiffness and rattle.

Nitrocellulose coatings which satisfy to a greater or less degree the requirements in these regards have been known for some time; textiles so coated generally being termed "artificial leather." However, nitrocellulose has certain inherent drawbacks as a textile coating, especially where the coated textile is eventually used for military purposes, such as equipment coverings, raincoats, etc. These drawbacks include, among others, inflammability and unsatisfactory flexibility at low temperatures.

Textiles coated with ethyl cellulose have been prepared, but there have been a number of objectionable features which have limited their utility. Poor adhesion has been encountered with numerous formulations, in addition to stiffening and poor handle, and particularly blocking at elevated temperatures. Furthermore, pigmenting the coatings caused embrittlement which led to cracking. In an effort to prevent stiffening and cracking, the plasticizer content has been increased, but as a result, adhesion to the textile fabric was lowered. Furthermore, the increase in plasticizer content caused blocking and exudation or stickiness at elevated temperatures.

The phenomenon which has caused the most severe limitations in utilizing cellulose ether coatings for textiles is that of exudation of plasticizers, particularly mineral or vegetable oils, from the usual types of cellulose ether coatings when

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the ether : plasticizer ratio is less than about 1:1. Alternatively, in some cases, extreme stickiness under warmth has resulted.

Now, in accordance with this invention, the shortcomings of the prior art have been substantially eliminated by providing a textile fabric with a combination of three types of compositions: First, a "wetting coat," which is a highly plasticized cellulose ether composition; second, a "toughening coat," which is a cellulose ether composition somewhat less highly plasticized; and third, a "sealing coat," which comprises a cellulose ether of a substitution type which will not permit any substantial penetration of the plasticizers of the other compositions through it.

The wetting coat is so applied that the interstices of the fabric are substantially closed, but a continuous coating on the surface of the fabric is not formed. The toughening coat is so composited and applied that it forms a continuous surface coating, but substantially no impregnation of the fabric occurs. These two compositions may be pigmented. The sealing coat contains a cellulose ether having a relatively low substitution and may contain a flatting agent.

The drawing accompanying this specification is a cross-sectional representation of the special relationships of a typical textile fabric coated with the three types of compositions in accordance with this invention. Fabric composed of threads 4 and 5 has its interstices substantially closed by a wetting coat 3. Superimposed on the wetting coat is a layer or coating 2 which may be referred to as the toughening coat. The uppermost coat is the sealing coat 1. It will be appreciated that each layer may be the result of application of several coats of composition.

Various embodiments of the invention are illustrated by the following specific examples: Table 1 contains 12 examples of wetting coats which may be applied to the textile fabric to fill the interstices thereof. Table 2 contains 13 examples of toughening coats which are applied over the wetting coat. Table 3 shows three sealing coat compositions. Finally, Table 4 gives 17 of the best combinations of the coats described in Tables 1, 2, and 3.

TABLE 1

Wetting coats

Example No.	1	2	3	4	5	6	7	8	9	10	11	12
Ethyl cellulose, 47.5 ethoxyl, 100 cp. viscosity	30	30	30	30	30	30	30	30	30	30	30	30
Chlorinated diphenyl						50	50				50	
Bodied castor oil, 200 seconds Engler viscosity			45	80								
Bodied castor oil, 400 seconds Engler viscosity		45			80							
Bodied castor oil, 1500 seconds Engler viscosity	45											
Raw castor oil	25	25	25				30	70	70	70	30	30
Corn oil						30						50
Hydrogenated methyl abietate												15
Olive drab pigment	12.5	12.5	12.5	15	15	15	15		7.5	12.5	15	15
Xylene	200	200	200	200	200			100	200	200	150	150
Butanol	90	90	90	90	90	50	80	40	90	90	60	60
Solvesso #2 (a hydrogenated petroleum fraction)						125	200					

TABLE 2

Toughening coats

Example No.	13	14	15	16	17	18	19	20	21	22	23	24	25
Ethyl cellulose, 47.5 ethoxyl, 100 cp. viscosity	50	50	50	40	40	40	40	40	40	50	50	50	40
Corn oil							60						
Bodied castor oil, 200 seconds Engler viscosity			25	60				30	30				
Bodied castor oil, 400 seconds Engler viscosity		25			60	30							
Bodied castor oil, 1500 seconds Engler viscosity	25												
Raw castor oil	25	25	25			30		30	30	50	50	50	30
Hydrogenated methyl abietate													
Olive drab pigment	12.5	12.5	12.5	15	15	15	15	15	15		7.5	12.5	15
Xylene	250	250	250	200	200	200			200	150	250	250	140
Butanol	100	100	100	80	80	80	85	85	80	60	100	100	60
Solvesso #2							200	200					

TABLE 3

Sealing coats

Example No.	26	27	28
Ethyl cellulose, 45% ethoxyl, 100 cp. viscosity	30		
Ethyl cellulose, 45% ethoxyl, 300 cp. viscosity		30	50
Zinc stearate		8	
Diphenylamine		0.38	
Xylene		250	475
Butanol	100	100	100
Solvesso #2	250		

TABLE 4

Best combinations of above coatings

Combination—Example No.	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Wetting Coat—Example No.	1	2	2	3	3	3	4	4	5	6	7	8	9	10	10	11	12
Toughening Coat—Example No.	13	14	18	13	15	21	16	16	17	19	20	22	23	23	24	25	25
Sealing Coat—Example No.	28	28	28	28	28	27	27	28	27	26	26	28	28	28	28	27	27

Example 46 shows the application to a textile fabric of compositions given under Examples 2, 18, and 27.

Example 46

A wetting coat dope of the composition under Example 2 of Table 1 was prepared by mixing the ingredients in a closed vessel equipped with a slow-moving agitator until a smooth dope was obtained. The pigment had previously been dispersed on a three-roll mill in a portion of the plasticizer in the ratio of 1 part pigment to 2 parts plasticizer. All composition figures in these examples are in parts by weight. The wetting dope obtained was then applied to cotton cloth weighing 4 ounces per yard by use of a doctor knife coater. Solvents were removed by drying at 100° C. Application had been adjusted so that 1.3 ounces of the dried composition were applied to 1 square yard of cloth. This amount was sufficient to fill the interstices of the cloth but not to leave any surface coating thereon.

A toughening coat dope of the composition under Example 18 of Table 2 was prepared in the same manner as the wetting coat dope above. The toughening coat dope was applied to the filled cloth with a doctor knife coater so as to deposit 1.3 ounces of solids in a continuous coating per square yard of the cloth. Solvents were removed as above.

A sealing coat dope of the composition under Example 27 of Table 3 was prepared by dissolving the ethyl cellulose in the solvent and adding the flatting agent and stabilizer during the latter stages of mixing. This was applied to the filled and coated cloth with a doctor knife coater adjusted to give a dry coating of 0.4 ounce per yard of cloth. Solvents were removed in the same manner as before.

The coated cloth had a soft handle, good drape, and was highly flexible. It was suitable for such a use as raincoat cloth. At −20° C., flexibility was satisfactory, while after heating at 180° F. for 30 minutes, as described hereinafter, there was no evidence of blocking.

While the examples show the use of ethyl cellulose in specific embodiments of the invention, and while this is the preferred cellulose ether for carrying out the invention, other cellulose ethers may be used. These include other alkyl ethers such as methyl, propyl or butyl; aralkyl ethers such as benzyl; carboxyl-alkyl ethers such as carboxymethylcellulose, especially when given a water-insolubilizing treatment; hydroxy-alkyl celluloses, such as hydroxyethyl cellulose, especially when water-insolubilized; and mixed ethers such as methyl ethyl, ethyl benzyl, and ethyl butyl ethers. It will be understood that water-soluble cellulose ethers, such as hydroxy-alkyl and carboxy-alkyl celluloses will ordinarily require an insolubilizing treatment, preferably after application to the textile.

The cellulose ethers for each coat must be carefully chosen so that the plasticizers used therewith in the wetting and toughening coats will not penetrate through the sealing coat. Thus, when the multiple coatings comprise ethyl cellulose as the cellulose ether, it is preferred that the ethoxyl of the cellulose ether be between about 40.0 and about 52.0% in the wetting coat and between about 44.5 and about 52% in the toughening coat, while that of ethyl cellulose in the sealing coat is preferably between about 40.0 and about 45.5%.

It has been found that the substitution of the cellulose ether in the wetting coat is not so important as the difference in substitution between the cellulose ether of the toughening coat and that of the sealing coat. This difference in substitution of the latter two coats is to be such as to prevent appreciable migration of the plasticizer of the middle coat into or through the sealing coat. The sealing coat cellulose ether will be less soluble in the plasticizer of the toughening coat than the cellulose ether of the toughening coat and may, in fact, be incompatible with said plasticizer.

To obtain the optimum conditions in this re-

spect when the cellulose ether is ethyl cellulose, the ethoxyl of the sealing coat is at least 1.3% less than that of the ethyl cellulose in the toughening coat. Preferably, a relatively high ethoxyl is used for the toughening coat in order to obtain maximum flexibility and compatibility with plasticizers.

It will be noted that the sealing coat thus comprises ethyl cellulose which has only a limited compatibility with plasticizers such as mineral oils or vegetable oils in the sense that they will repel said plasticizers back into the more compatible types of ethyl cellulose in the wetting and toughening coats instead of allowing them to penetrate through and exude from the sealing coat, or mix with and cause blocking of said coat.

The viscosities of the cellulose ethers to be used in the three types of coats may vary within wide limits. The dope must have a composite viscosity suitable for application with a particular type of coating apparatus.

It has been found that the viscosity of the cellulose ether in the wetting and toughening coats may vary between about 50 and about 300 centipoises, and preferably is about 100 centipoises. The viscosity of the cellulose ether in the sealing coat may vary from about 100 centipoises to about 500 centipoises and preferably is about 300 centipoises.

The present invention permits the employment, as textile coatings, of highly plasticized cellulose ethers in the wetting and toughening coats. Examples 1–12 show ethyl cellulose:plasticizer ratios in wetting coats varying from 1:2.3 to 1:2.7. While this is the preferred range of ratios in the wetting coat, the ratio may vary from about 1:1 to about 1:3.5. Examples 13–25 show toughening coats containing ethyl cellulose:plasticizer ratios of about 1:1 to 1:1.5. This is the preferred ratio range for the toughening coat, but ratios in said coat may vary from about 3:1 to about 1:2. As shown by Examples 26, 27, and 28 in Table 3, it is a preferred practice to use no plasticizer whatever in the sealing coat. However, a limited amount of plasticizer may be used therein, but the cellulose ether:plasticizer ratio should be greater than about 3:1.

A wide range of plasticizers may be used in carrying out the present invention. As shown by Examples 1–25, chlorinated diphenyl, hydrogenated methyl abietate, corn oil, raw castor oil, and bodied castor oil are especially suitable. Other plasticizers which may be used include mineral oils such as Nujol or refined types of lubricating oil; other vegetable oils such as cottonseed, linseed, or soybean oils; fatty acids such as oleic or stearic acids; amides such as para-toluene-sulfonamide; phosphate esters such as tricresyl phosphate, or triphenyl phosphate, phthalate esters such as dimethyl phthalate, or dibutyl phthalate; and carbohydrate derivatives such as mannitol propionate, or sorbitol propionate.

The plasticizers preferred above others in carrying out the present invention are chlorinated diphenyl, raw castor oil, and lightly-bodied castor oil. When castor oils are the plasticizers used, it is a preferred practice to use mixtures of raw and lightly-bodied varieties. Raw castor oil promotes flexibility of the coatings while the bodied oil promotes adhesion.

The raw vegetable oils may be bodied by various means such as heating or oxidizing. Oxidation is usually accompanied by polymerization and since highly polymerized oils impart low temperature brittleness to a coating, it is preferred to utilize only such oxidized oils as have been polymerized to a relatively mild degree. By the aforesaid term, vegetable oils polymerized by other means are also included, for example, by heat. The term vegetable oil also includes mixtures of the vegetable oils mentioned hereinbefore. However, it is preferred practice to utilize raw castor oil or castor oil which has been slightly polymerized by oxidation as the vegetable oil softener of this invention.

This softener may be, for example, castor oil which has been oxidized and, at the same time, polymerized to such an extent as to change its viscosity from the original 130 seconds Engler to 400 seconds Engler, such as the oil known as "Baker's Pale No. 4 Castor Oil." Another useful type of oil for the purpose of the present invention has received a lighter bodying treatment to give a viscosity of about 200 seconds Engler, such as the castor oil known as "Baker's 2AC Oil." Oils having a higher degree of bodying are also useful for this invention. A specific example of such an oil is known as "Baker's #16 Pale Blown Castor Oil," having an Engler viscosity of about 1500 seconds viscosity.

Pigments other than the olive drab pigment, shown in the examples, may be used in the coatings of the present invention. As shown by the examples, it is a preferred practice to apply the pigment in the wetting and toughening coats, while the sealing coat is preferably a clear one. Although the preferred cellulose ether : pigment ratio range is between about 4:1 to about 2:1 in the wetting coat, said ratio may vary from about 6:1 to about 3:2. As shown by Examples 13–25, the preferred cellulose ether : pigment ratio range in the toughening coat is from about 6.1:1 to about 2.7:1, the ratio range may vary from about 8:1 to about 2:1. Although it is a preferred practice to omit pigment from the sealing coat, cellulose ether: pigment ratios greater than about 4:1 are permissible. Flatting agents other than the zinc stearate shown in Example 27 include diatomaceous earth, magnesium carbonate, and aluminum stearate.

It will be understood that there may be considerable variation in the weight of coatings applied for various purposes. For raincoat material made of a fabric such as that shown in Example 46, it is preferred that the wetting and toughening coats weigh from about 1.2 to about 1.5 ounces per square yard and that the sealing coat weigh from about 0.3 to about 0.5 ounce per square yard. However, coated fabrics may be made according to the present invention bearing coating weights commensurate with their intended use. It is preferred practice to apply a sealing coat of considerably less weight than the wetting or toughening coats so as to avoid stiffening.

While the examples show the application of the several coats to the fabric in the form of dopes, it is within the contemplation of this invention that said coats be applied as hot melts by use of a roll mill, doctor knife, or calender stack. This hot melt method would be particularly suitable for the wetting and toughening coats, since they contain large amounts of plasticizer. If applied in dope form, the consistency of the dope may be adjusted for spray, brush, or doctor knife application. Solvents will necessarily be removed after applying one coat before the next is applied.

It is also within the contemplation of this in-

vention to use more than one coat of each of the three types. Thus, a heavier coating may be built up, if desired, in a stepwise manner, rather than applying all of one type of coating in a single treatment.

Resistance to low temperature is tested by subjecting the coated fabric to a temperature of −20° F. for 30 minutes and then folding the fabric at that temperature. Examination is then made for cracking or flaking.

Blocking is measured by folding a piece of the fabric over on itself, placing it between glass plates and loading with a 1-pound weight. After 30 minutes at 180° F. and cooling for 5 minutes, the folded fabric is pulled apart to note blocking. A piece which opens without any effort or noise is free of blocking. A crackling noise without visible picking or cohesion of the coating to itself is regarded as indicating slight blocking. Prior art coatings may block badly enough to coalesce.

Adhesion may be estimated by two tests. In the first, the coating is scrubbed vigorously over itself and the number of scrubbing motions necessary to rupture the film is noted. In the other, the coated fabric is torn, using a pull nearly parallel with the surface, and the edges of the tear observed. Ragged edges denote poor adhesion, while a coating which severs exactly with the tear is said to have good adhesion. Multiple coatings made according to the present invention have numerous advantages over the prior art, in that they are substantially noninflammable as compared with nitrocellulose coatings; are designed to contain relatively large proportions of plasticizers in the wetting and toughening coats, but at the same time will not block or exude plasticizers, due to the presence of the sealing coat.

Wherever viscosity of ethyl cellulose is referred to throughout the examples, specification, and claims, it will be understood to mean centipoises viscosity in 80–20 toluene-alcohol mixtures measured at 25° C. containing 5% ethyl cellulose by weight.

What I claim and desire to protect by Letters Patent is:

1. A textile fabric bearing a flexible, nonblocking multiple coating comprising: a wetting coat comprising ethyl cellulose having an ethoxyl content between about 40.0 per cent and about 52.0 per cent by weight and a plasticizer, the ethyl cellulose:plasticizer ratio being in the range between about 1:1 and about 1:3.5, said wetting coat substantially closing the interstices of said fabric without forming a continuous coating thereon; a toughening coat comprising ethyl cellulose having an ethoxyl content between about 44.5 per cent and about 52.0 per cent by weight and a plasticizer, the ethyl cellulose:plasticizer ratio being in the range between about 3:1 and about 1:2 but substantially greater than that of the wetting coat composition; said toughening coat forming a continuous coating on the surface of said fabric and tightly adhering thereto with substantially no impregnation thereof; and a sealing coat superimposed upon the toughening coat and comprising an ethyl cellulose having an ethoxyl content between about 40.0 per cent and about 45.5 per cent by weight, the ethoxyl content of the ethyl cellulose in said sealing coat being lower than the ethoxyl content of the ethyl cellulose in said toughening coat by at least 1.3 per cent, whereby substantial migration therethrough of the plasticizers of the wetting and toughening coats is prevented.

2. A textile fabric bearing coatings according to claim 1, in which the plasticizer comprises chlorinated diphenyl.

3. A textile fabric bearing coatings according to claim 1, in which the plasticizer comprises raw castor oil.

4. A textile fabric bearing coatings according to claim 1, in which the plasticizer comprises bodied castor oil.

5. A textile fabric bearing coatings according to claim 1, in which the top coating contains a flatting agent.

6. A textile fabric bearing coatings according to claim 1, in which the top coating contains zinc stearate.

7. A textile fabric bearing coatings according to claim 1, in which the ethyl celluloses which comprise the first two coatings have viscosities between about 50 and about 300 centipoises when measured at 25° C., in 5% solution of 80-20 toluene-alcohol.

8. A textile fabric bearing coatings according to claim 1, in which the ethyl cellulose which comprises the top coating has a viscosity between about 100 and about 500 centipoises when measured at 25° C. in 5% solution of 80–20 toluene-alcohol.

9. A textile fabric bearing a flexible, nonblocking multiple coating comprising: a wetting coat comprising ethyl cellulose having an ethoxyl content between about 40.0 per cent and about 52.0 per cent by weight and a plasticizer, the ethyl cellulose:plasticizer ratio being in the range between about 1:2.3 and about 1:2.7, said wetting coat substantially closing the interstices of said fabric without forming a continuous coating thereon; a toughening coat comprising ethyl cellulose having an ethoxyl content between about 44.5 per cent and about 52.0 per cent by weight and a plasticizer, the ethyl cellulose:plasticizer ratio being in in the range between about 1:1 and about 1:1.5, said toughening coat forming a continuous coating on the surface of said fabric and tightly adhering thereto with substantially no impregnation thereof; and a sealing coat superimposed upon the toughening coat and comprising an ethyl cellulose having an ethoxyl content between about 40.0 per cent and about 45.5 per cent by weight, the ethoxyl content of the ethyl cellulose in said sealing coat being lower than the ethoxyl content of the ethyl cellulose in said toughening coat by at least 1.3 per cent, whereby substantial migration therethrough of the plasticizers of the wetting and toughening coats is prevented.

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