

UNITED STATES PATENT OFFICE

2,431,001

COATED FABRIC

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No Drawing. Application April 27, 1945,
Serial No. 590,715

11 Claims. (Cl. 117-76)

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This invention relates to an improved process for coating fabrics which are particularly adapted for upholstery purposes.

A great variety of coating compositions and systems have been employed in the manufacture of coated fabrics designed particularly for use as upholstery coverings in the construction of furniture, transportation vehicles including pleasure automobiles, trucks, busses, railway cars and the like where requirements with respect to appearance and general durability, particularly wear resistance, are exceedingly severe. Compositions based on varnishes, cellulose derivatives, rubber and synthetic resinous materials have been used in finishing systems for the manufacture of upholstery but have been deficient in one or more of the essential requirements of flexibility, adhesion, toughness, durability on outdoor exposure, resistance to staining and retention of elasticity on aging.

This invention has as an object the provision of a system for manufacturing upholstery which affords a finished product of markedly superior properties. Another object is the provision of an upholstery finishing system in which the top coat is susceptible to controlled halogenation, thus affording a durable, "case-hardened" finish with improved surface slip. Another object is the provision of finishes, particularly adapted for the manufacture of upholstery, which are resistant to staining from oils, greases, cosmetics and foodstuffs. Another object is the provision of upholstery finishes which are remarkably wear resistant. Another object is the provision of upholstery finishes which are characterized by superior durability, when exposed outdoors and which are distinguished by outstanding resistance to heat, light, oxidation and cracking at low temperatures. Another object is the provision of a finish which affords better definition of grain when embossed and which retains the grain for longer periods of time. A further object is the provision of finishes for fabrics which are tough and flexible and which afford superior aging properties. A further object is the provision of finishes for fabrics which are highly adherent to the fabric substrate. A still further object is the provision of finishes for fabrics which afford improved resistance to water and to abrasion. Other objects will become apparent as the description of the invention proceeds.

These objects are accomplished in accordance with the present invention, by means of a plurality of coatings comprising at least one coating containing an elastomer selected from the group

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consisting of rubber, sulfur modified chloroprene (chloro-2-butadiene-1,3), acrylonitrile-butadiene interpolymers (Hycar, Perbunan), and butadiene-styrene interpolymers (Buna S) and a top-coat containing a chloroprene (neoprene)-acrylonitrile interpolymers, preferably containing about 18 percent acrylonitrile, as essential ingredients, applied to a fabric substrate and subsequently halogenated.

The following examples are given by way of illustration only and no limitations are intended thereby except as indicated in the appended claims.

Cotton duck sateen weighing about one pound per 54" yard was base coated by means of conventional spreader application with about two ounces per square yard of the following composition:

Example 1

	Percent by weight
Neoprene-----	89.6
Accelerator-softener ¹ -----	1.3
Anti-oxidant (MUF) ² -----	0.3
Zinc oxide-----	3.8
Magnesium oxide-----	3.5
Stearic acid-----	1.0
Benzothiazyl disulfide (accelerator)-----	0.5
	100.0

¹The accelerator-softener consisted of Latac (hexamethylene ammonium hexamethylene-dithiocarbamate).

²The anti-oxidant consisted of N, p-tolyl N', p-tolyl sulfonfyl p-phenylene diamine manufactured and sold by Naugatuck Chemical Company as MUF. Other conventional anti-oxidants such as di-beta-naphthol para phenylene diamine can be substituted however for the MUF with satisfactory results.

The neoprene used in this example was a sulfur modified chloroprene containing about 0.75 percent of sulfur prepared in accordance with the procedures described in U. S. Patent 2,264,173, particularly Example 25.

The composition was prepared by the conventional process of combining the materials in a heavy duty kneading machine, such as a Banbury mixer after which it was dissolved in xylene (approximately 40 parts of composition to 60 parts of xylene) to spreader viscosity by mixing in an agitator mixer.

The fabric carrying the above described uncured base coat was then calender coated in an amount of about 9½ ounces of the following composition which was prepared as in Example 1 by combining the materials in a heavy duty kneading machine such as a Banbury mixer.

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Example 2

	Percent by weight
Neoprene	33.90
Accelerator-softener	.06
Stearic acid	.18
Crown clay	36.80
Anti-oxidant (MUF)	.12
Chrome tanned ground leather	9.67
Red lake (azo pigment dyestuff)	1.94
Chrome yellow pigment	1.94
Red lake (precipitated azo pigment dye-stuff)	1.94
"Circo" oil	2.91
Titanium-calcium pigment	4.84
Zinc oxide	1.45
Magnesium oxide	1.45
Dibutyl ammonium oleate	2.90
	100.00

The neoprene, accelerator-softener and anti-oxidant used in this composition were of the same type as described in Example 1. The "Circo" oil is a petroleum process oil of low aniline point.

Immediately following the application of the Example 2 coating, a top coat of the following composition thinned to spreader viscosity in a proportion of about 40 parts by weight of the composition to 60 parts of a solvent consisting of nitropropane was applied in an amount of about 1/2 ounce per square yard by conventional knife coating process.

Example 3

	Percent by weight
Neoprene (chloroprene-acrylonitrile interpolymer)	38.56
Anti-oxidant (MUF)	.13
Red lake (azo pigment dyestuff)	2.20
Chrome yellow	2.20
Red lake (precipitated azo pigment dye-stuff)	2.20
"Circo" oil	3.31
Titanium-calcium pigment ("TiCal")	5.51
Crown clay	41.88
Zinc oxide	1.65
Magnesium oxide	1.52
Stearic acid	.42
Benzothiazyl disulfide ("Altax")	.21
Sulfur	.21
	100.00

This composition was prepared by combining the materials on a rubber roller mill after which the homogeneous mixture was dissolved in nitropropane in the proportions previously indicated in a high speed agitator mixer.

The chloroprene-acrylonitrile interpolymer used in this example which contains about 18% acrylonitrile may be prepared in accordance with the procedure described in U. S. Patent 2,066,331 (Carothers et al.).

The coated fabric was embossed and then oven cured by heating for 2 1/2 hours at 260° F.

The top coating (Example 3) was halogenated by treatment with a solution containing 6 percent sulfur chloride and 6 percent bromine in carbon tetrachloride followed by a treatment with a carbon tetrachloride solution containing 20 percent bromine. These treatments may be applied by brushing, dipping, flow application or other convenient means.

After the halogenation treatments, the coated fabric is passed through a chamber saturated with water vapor from low pressure steam and maintained at a temperature of about 140° F.

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Commercial grade ammonia is fed into the chamber at the rate of two pounds per minute. The total neutralizing cycle was four minutes.

The upholstery material finished as described above exhibits exceptionally high-resistance to the abrasion, flex and scrub tests to which such materials are usually subjected. The new product was particularly distinguished by its marked superiority in edge wear resistance, a property which is of great importance in upholstery constructions using a beading. The improved system also was found to afford excellent resistance to deterioration from exposure to sunlight. General durability on outdoor exposure was outstanding and a decided improvement in resistance to crocking as determined by rubbing with a wet cloth was observed. The finish exhibited desirable surface slip and excellent resistance to staining.

In the examples, a combined sulfur chloride and sulfur-chloride-bromine treatment is described. However, it is also possible to employ other halogenation treatments. For example, it has been found that in some cases, notably where the top coat consists of chloroprene-acrylonitrile interpolymer (Example 3) halogenation with bromine alone affords ever superior results.

The following composition was also found to be suitable as an intermediate coating in the present invention and was prepared and applied as described above for Example 2.

Example 4

	Per cent by weight
Neoprene (0.75% sulfur modified chloroprene)	36.00
Accelerator (dibutyl ammonium oleate)	.91
Refined paraffin wax	.91
Stearic acid	.20
Zinc oxide	15.50
"Kalite" (stearic acid treated calcium carbonate)	14.40
Shellac	8.22
Ground chrome tanned leather	10.30
"Circo" oil	3.10
Magnesium oxide	1.42
Anti-oxidant (MUF)	.14
Red lake (azo pigment dyestuff)	.64
Lead chromate yellow pigment	8.23
Channel black	.03
	100.00

As a top coat for the new finishing system, the following composition also provided excellent results particularly when used in conjunction with the intermediate coating of Example 4.

Example 5

	Per cent by weight
Neoprene (chloroprene-acrylonitrile interpolymer)	38.00
Anti-oxidant (MUF)	.15
"Circo" oil	3.25
Zinc oxide	16.25
"Kalite"	15.18
Shellac	8.58
Magnesium oxide	1.50
Stearic acid	.42
"Altax" (Benzothiazyl disulfide)	.21
Sulfur	.21
Monastral blue pigment	3.25
Red iron oxide	.28
Lead chromate yellow pigment	10.00
Channel black	2.72
	100.00

5 This composition was prepared and applied over the intermediate composition of Example 4 in accordance with the procedure of Example 3. This coating was then halogenated by treatment with a 20 percent solution of bromine and neutralized as in Example 3.

The use of shellac in the composition of Examples 4 and 5 provides a finish that is somewhat more rigid in the uncured state and sets quickly after leaving the calender rolls. It is not subject to cold flow and gives particularly good embossing definition. The shellac and "Kalite" modification also seems to further reduce chalking and crocking on extended exposures.

The following examples illustrate other undercoat systems which may be employed with satisfactory results in combination with the halogenated topcoat based on a chloroprene-acrylonitrile interpolymers such as Example 3. The system described in Examples 1, 2 and 3 however is preferred.

Example 6.—Base coat

	Per cent by weight
Butadiene-styrene interpolymers (Buna S) ..	77.0
"Galex" (hydrogenated rosin) ..	15.4
Cumar resin ..	7.6
	100.0

The composition of Example 6 was applied to cotton duck sateen as in Example 1 and then calender coated with the following composition as an intermediate coating, applied as in Example 2 and top-coated with the composition of Example 3 which was subsequently halogenated.

Example 7.—Intermediate coat

	Per cent by weight
Butadiene-styrene interpolymers (Buna S) ..	35.70
Zinc oxide ..	15.30
"Kalite" (stearic acid treated calcium carbonate) ..	41.00
2-mercaptotriazoline ..	.50
"Thionex" (tetramethyl-thiuram - monosulfide) ..	.25
"Barak" (dibutyl ammonium oleate) ..	.38
Sulfur ..	.76
Red lake (azo pigment dyestuffs) ..	6.11
	100.00

The following composition may be substituted directly for Example 2 as an intermediate coating using the base coat of Example 1 and the topcoat of Example 3.

Example 8.—Intermediate coat

	Per cent by weight
Butadiene-acrylonitrile interpolymers ("Perbunan") ..	34.80
Ground leather ..	11.80
Zinc oxide ..	4.90
Red lake (azo pigment dyestuff) ..	5.90
Stearic acid ..	.24
Crown clay ..	40.80
Plasticizer (processed mineral oil) ..	.50
Accelerator ("Zenite") ¹ ..	.50
"Thionex" (tetramethyl-thiuram-monosulfide) ..	.06
Sulfur ..	.50
	100.00

¹90% zinc salt of 2-mercaptobenzothiazole and 10% hydrocarbon wax.

A system employing a base coat and an intermediate coating based on rubber may also be employed in conjunction with a topcoat such as Example 3 which is halogenated after its application as described above.

Example 9.—Base coat

	Percent by weight
Rubber ..	70.0
Zinc oxide ..	10.0
Rosin ..	9.0
Barytes ..	11.0
	100.0

15 An anti-oxidant consisting of N, p-tolyl N', p-tolyl sulfonyl p-phenylene diamine manufactured and sold by the Naugatuck Chemical Company as MUF was added in the proportion of 4 ounces for each 100 pounds of the above composition.

20 An intermediate coating consisting of the following composition may be calender coated over the base coat of Example 9 and finally the topcoat of Example 3 applied and halogenated as previously described.

Example 10.—Intermediate coat

	Percent by weight
Rubber ..	34.43
Montan wax ..	6.27
Ground leather ..	15.65
Zinc oxide ..	15.65
"Kalite" (stearic acid treated calcium carbonate) ..	16.70
Red lake (azo pigment dyestuff) ..	9.40
Accelerator ("Zenite") ¹ ..	.46
"Thionex" (tetramethyl-thiuram-monosulfide) ..	.20
"Barak" (dibutyl ammonium oleate) ..	.20
Antioxidant (MUF) ..	.27
Sulfur ..	.77
	100.00

¹90% zinc salt of 2-mercaptobenzothiazole and 10% hydrocarbon wax.

It is essential that the top coat be readily susceptible to halogenation to provide a hard, wear resistant surface and for this purpose the chloroprene-acrylonitrile interpolymers are particularly outstanding. The sulfur modified neoprene which finds particular merit as an undercoat in the present system and other synthetic elastomers such as butadiene-styrene interpolymers are difficult to halogenate and therefore are not suited for top coatings in the improved finishing system. However, for undercoats, including base coats, they are satisfactory and contribute many important and necessary properties to the overall superiority of the system. Thus the base coat and intermediate undercoats may consist of compositions containing acrylonitrile-butadiene interpolymers (Hycar, Perbunan), butadiene-styrene interpolymers (Buna S), rubber, sulfur modified neoprene or other such elastomers which are compatible with the special topcoat containing chloroprene-acrylonitrile interpolymers.

The thickness or weight of the several coatings in the present finishing system is important, particularly with respect to the top-coat. For most purposes, a coating weight of the chloroprene-acrylonitrile interpolymers composition (Example 3) of about 0.5 ounce per square yard is preferred. When this coating weight is reduced much below 0.25 ounce per square yard

the abrasion resistance of the finish is unsatisfactory. In general, the coating weight of the top-coat need not exceed about 1.0 ounces per square yard. Also there is not much to be gained in the desired wear resistance with top coating weights substantially above this amount. The filler content of the top-coat composition is also somewhat controlling in the coating weight and the above weights are based on a preferred filler content of about one part by volume of filler to about one to three parts by volume of chloroprene-acrylonitrile interpolymers. If the composition is more heavily loaded with filler then the top coating weight should be correspondingly increased. Although a total coating weight of about 11½ ounces is shown in the examples for the undercoats and is preferred in about this amount for upholstery purposes, coating weights of the undercoats on the order of about two ounces per square yard may be used for garment

The coating system is not limited to any particular type of fabric but may be employed with various supporting base fabrics, including cotton fabric (duck, sateen, etc.), nylon, Fibre A, paper, rayon, etc.

The unique improvements afforded by the present invention may be attributed to the cooperative arrangement of the different coatings to provide the superior qualities in upholstery and related products. This is accomplished presently by means of a combination of a plurality of coatings in such relation that each contributes vitally to the attainment of long sought objectives. Thus the particular types of undercoats described in Examples 1 and 2 which form the major part of the entire coating provide retained flexibility and exceptional resistance to atmospheric aging, especially light and heat exposure periods. The relatively thin halogenated top coat which comprises compositions such as Examples 3 and 5 provides a means for controlling halogenation to only a surface effect. These specific types of elastomers are much more susceptible to halogenation than the previously described under-coat compositions and because of their more receptive nature to this treatment prevent the undercoats from reacting to any appreciable degree with the halogen. The chloroprene-acrylonitrile interpolymers top-coats when thus treated afford a surface which is smooth and hard and which is outstanding in its resistance to wear. It appears that in the process of the invention there is a more complete halogenation on the outer or exposed surface which is progressively less beneath the surface and toward the interface of the undercoats and the top-coat so that at the interface there is excellent adhesion of these coatings which are cured together to give a more unitary structure thus reducing tendency for separating while maintaining the desired hard wear resistant top surface. The combination of coatings in the specific order described afford many other importantly essential properties for upholstery purposes.

The primary utility of the new finishing system involves the manufacture of upholstery products where the superior properties provided are most desirable. The improved upholstery is particularly suited for beading in upholstery construction where resistance to edge wear is essential. However, the invention is likewise ap-

plicable to the coating of fabrics and other flexible and semi-rigid, porous bases such as paper, for a wide variety of purposes, including automobile top material, shoe parts, such as shoe counters, caps and uppers and as material for bookbinding.

The present invention is characterized by numerous important advantages. A remarkably high degree of resistance to wear in upholstery construction has been achieved. The new coatings afford exceptional durability on outdoor exposures and are highly resistant to deteriorating effects of actinic light, heat and oxidation. The definition of grain when the coating has been embossed surpasses that obtained with more conventional finishes and this definition is also retained for more extended periods. The surface of the finish is smooth and abrasion resistant. It is also highly flexible and resistant to crocking at low temperatures. The finish is substantially non-staining from contact with cosmetics and foodstuffs and is practically unaffected by oils and greases. The new system provides for controlled halogenation so that only a thin surface film is "case-hardened" and the remainder of the coating is not affected thus retaining the desirable contributing properties of the undercoats. The finish is also noteworthy for its absence of "wet-crocking" or chalking after long exposures. It is also tough and highly water resistant and withstands flexing and scrubbing to an unusual degree.

As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof it is therefore not intended to be limited except as indicated in the appended claims.

I claim:

1. An improved process for coating fabrics comprising applying at least one coat of a composition containing an elastomer selected from the group consisting of rubber, chloroprene, acrylonitrile-butadiene interpolymers and butadiene-styrene interpolymers to a fabric substrate, thereafter applying a topcoat of a composition containing a chloroprene-acrylonitrile interpolymers, curing the coatings and thereafter halogenating the said topcoat with material selected from the group consisting of chlorine and bromine, the said interpolymers containing about 18% of acrylonitrile.
2. An improved process for coating fabrics comprising applying a plurality of coatings to a fabric substrate consisting of a size coating, an intermediate coating and a top coating, curing and subsequently halogenating the top coating with material selected from the group consisting of chlorine and bromine, the said size coating and intermediate coatings comprising an elastomer selected from the group consisting of rubber, chloroprene, acrylonitrile-butadiene and butadiene-styrene interpolymers and the said topcoat comprising an interpolymers of chloroprene-acrylonitrile said interpolymers containing about 18% of acrylonitrile.
3. Process of claim 2 in which the size coating and intermediate coating comprise a sulfur modified chloroprene and the topcoat comprises a chloroprene-acrylonitrile interpolymers.
4. Process of claim 2 in which the halogenation comprises treatment with bromine.
5. Process of claim 2 in which the halogenation comprises treatment with bromine and sulfur chloride.
6. A fabric carrying a plurality of coatings in-

cluding at least one undercoat and a topcoat, the said undercoat comprising an elastomer selected from the group consisting of rubber, chloroprene and interpolymers of acrylonitrile-butadiene and butadiene-styrene and the said topcoat comprising a chloroprene-acrylonitrile interpolymers surface halogenated with material selected from the group consisting of chlorine and bromine, said interpolymers containing about 18% of acrylonitrile.

7. Product of claim 6 in which the undercoats are present in an amount of about 11.5 ounces per square yard and the topcoat in amount of about 0.5 ounce per square yard.

8. An improved upholstery fabric carrying a plurality of coatings consisting of a size coat, an intermediate coat and a halogenated topcoat, the said size coat and intermediate coats comprising an elastomer selected from the group consisting of rubber, chloroprene, and interpolymers of acrylonitrile-butadiene and butadiene-styrene and the said topcoat comprising a chloroprene-acrylonitrile interpolymers surface halogenated with material selected from the group consisting of chlorine and bromine, said interpolymers containing about 18% of acrylonitrile.

9. Product of claim 8 in which the size coat and intermediate coat comprise a sulfur modified chloroprene and the topcoat comprises a halogenated chloroprene-acrylonitrile interpolymers.

10. Product of claim 8 in which the size coat is present in an amount of about two ounces per square yard, the intermediate coat in amount of about 9.5 ounces per square yard and the topcoat in an amount of about 0.5 ounce per square yard.

11. A fabric carrying a plurality of coatings including at least one undercoat and a topcoat, the said undercoat comprising an elastomer selected from the group consisting of rubber, chloroprene and interpolymers of acrylonitrile-butadiene and butadiene-styrene and the said topcoat comprising shellac and a chloroprene-acrylonitrile interpolymers surface halogenated with material selected from the group consisting of chlorine and bromine, said interpolymers containing about 18% of acrylonitrile.

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