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ARTIFICIAL LEATHER

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This invention relates to improved artificial leather and more particularly to artificial leather containing nitrocellulose and which is capable of retaining its flexibility at low temperatures and of retaining its softener at high temperatures.

Artificial leather consists of a flexible base and a pigmented coating of nitrocellulose softened chiefly by a vegetable oil, usually castor oil. Castor oil imparts an excellent resilience to the coating and is therefore generally used. However, artificial leather utilizing it has not been wholly satisfactory for some purposes, such as for automobile upholstery, because of two related defects. One is that upon exposure to the sun in very hot weather, the heat absorbed causes oil to exude from the coating. The second and more serious defect is that in very cold weather, the coating becomes brittle. The defect of exudation has heretofore been overcome by the use of polymerized oils for all or part of the softener or by the addition of solvent plasticizers. These measures not only increase the cost of the product but they also increase the tendency of the coating to become brittle upon being cooled. Thus, it may be seen that artificial leather would be greatly enhanced in value, if exudation at high temperatures could be prevented and at the same time flexibility at low temperatures could be improved. To accomplish this is an object of this invention.

Now, in accordance with my invention, the tendency of artificial leather coatings to exude softener upon being heated is eliminated and at the same time the temperature at which the coating becomes embrittled upon being cooled is appreciably lowered. I have further found in my invention a way of improving the durability of the product.

Briefly stated, an artificial leather in accordance with my invention comprises a moderately heavy web-like flexible base and thereon a flexible coating comprising a mixture of nitrocellulose with ethyl cellulose which is soluble in the usual organic solvents and a vegetable oil softener compatible with the said cellulosic mixture. Pigments or fillers or both may be included in the coating. Softener mixtures compatible with the said cellulosic mixture such as a mixture of a vegetable oil softener with another softener may be utilized.

By the term, a vegetable oil softener compatible with the cellulosic mixture, I include raw vegetable oils such as, for example, castor oil, soy bean oil, and the like, and oxidized vegetable oils

such as, for example, oxidized castor oil, oxidized soy bean oil, oxidized cottonseed oil, and the like. Oxidation is usually accompanied by polymerization and since highly polymerized oils impart low temperature brittleness to a coating, it is preferable to utilize only such oxidized oils as have been polymerized to a relatively mild degree. By the aforesaid term I also include vegetable oils slightly polymerized by other means, for example, by heat, but it is to be noted that oils polymerized more than slightly by heat alone do not fit the said term as they are incompatible with the cellulosic mixture. By the term, a vegetable oil softener, I also include mixtures of the vegetable oils mentioned hereinabove. However, I prefer to utilize raw castor oil or castor oil which has been slightly polymerized by oxidation as the vegetable oil softener of this invention.

The nitrocellulose utilized in the coating is one soluble in the usual artificial leather solvents. Preferably, it has a nitrogen content of about 11% to about 12.6%. Its viscosity is preferably above that of the type known as "RS 100 Second Nitrocellulose" but a useful artificial leather can be made with 15 second nitrocellulose or lower viscosity nitrocellulose, although the toughness of the coating decreases as viscosity is lowered.

The ethyl cellulose which I utilize in the coating of my improved artificial leather is one soluble in the usual organic solvents of the art, that is, one with an ethoxy content in the range of about 41% to about 51%. Preferably the ethoxy content is in the range of about 44 to about 48%. The viscosity, as in the case of the nitrocellulose, is preferably high so as to obtain maximum toughness. It is preferable, for example, to utilize an ethyl cellulose with a viscosity of about 60 to about 80 seconds or above about 60 seconds, as measured by the number of seconds required for a $\frac{1}{16}$ " steel ball to fall through 10 inches of a 20% solution of the ethyl cellulose in a solvent consisting of 80 parts toluene and 20 parts ethyl alcohol, the solution being maintained at 25° C. in a tube one inch in inside diameter.

The moderately heavy web-like flexible base of my artificial leather is any one of the usual artificial leather bases such as a cotton or other cloth of sheeting, sateen, broken twill, etc. construction, or such as a fibrous felt of similar thickness or a latex impregnated felt, and so forth. Such bases generally vary in weight from about 3 ounces to about 12 ounces per square yard.

The improved artificial leather in accordance with my invention may have, for example, from

about 3 ounces to about 14 ounces, say about 8 ounces, dry weight of the coating composition deposited per square yard of the flexible base. This coating will comprise, for example, a mixture of nitrocellulose and ethyl cellulose, both of which have been hereinbefore described, in the proportion such that from about 10% to about 80%, preferably from about 30% to about 60% by weight of the said mixture will consist of the ethyl cellulose. This cellulosic mixture will be flexibilized desirably by an amount of a vegetable oil softener of the type hereinbefore mentioned within the range of about 90% to about 250%, preferably within the range of about 100% to about 160%, by weight of the said cellulosic mixture. It will be appreciated that the softness of the coating may be varied as desired by varying the amount of softener. Preferably, the coating will be pigmented.

An artificial leather according to this invention has little tendency to exude softener upon being heated as by the sun in very hot weather; it surpasses in flexibility in the cold an artificial leather heretofore considered best in low temperature flexibility, namely one with a coating consisting of pigment, nitrocellulose, and raw castor oil; and it achieves these desirable properties utilizing as softener only raw castor oil, which is probably the cheapest softener of this art.

The manner in which these improvements are brought about is not clearly understood. My researches lead me to believe that the mixture of nitrocellulose with ethyl cellulose forms, with such an oil as castor oil, a gel structure which is quite different from the gels formed by either of the two cellulose derivatives singly with castor oil. This new, different gel structure has the rubbery resilience and freedom from stickiness desired and in addition its properties are much less affected by changes in temperature.

As has been indicated, I prefer in general to utilize raw castor oil as the softener of my artificial leather and I obtain a durable product therewith. However, I have found that further improvement in durability under the conditions of exposure to sunlight, may be obtained by the utilization of an oxidized oil, slightly polymerized, as the softener. 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." It will be appreciated that the use of highly polymerized oils reduces flexibility in the cold. Nevertheless, utilizing the oxidized polymerized oil just described, a product according to this invention can be obtained which is similar in flexibility at low temperatures to the best of the prior art and which is at the same time greatly superior in durability.

The softener utilized in the coating of my artificial leather may consist of one of the vegetable oil softeners hereinbefore mentioned, or a mixture of two or more thereof, or it may comprise in addition other softeners, provided that the mixture of softeners is compatible with the aforesaid cellulosic mixture used therewith. For example, it may be desired to include a resinous softener of high opacity to ultraviolet light, or a resinous softener imparting gloss, or a softener such as tricresyl phosphate and the like. When a mixture of softeners is used, the combined softener in general will be used in about the same proportion to the cellulosic mixture as herein-

before mentioned for a vegetable softener alone.

The flexible coating may include the fillers and pigments usual in artificial leather. Desirably, I utilize pigments high in covering power such as, for example, titanium dioxide, and especially pigments which are also highly opaque to ultraviolet light such as, for example, lead titanate and carbon black.

The artificial leather in accordance with this invention may be prepared by any of the common methods of the art. Conveniently, a coating dope is prepared by mixing an alcohol-wet nitrocellulose, ethyl cellulose, softener or softeners, pigment paste made by dispersing pigment in a portion of the softener, and solvents in a vessel equipped with suitable means of agitation until a smooth dope is obtained. The solvents may be similar to the usual nitrocellulose coating solvents such as, for example, a mixture of 30% ethyl acetate, 20% alcohol, and 50% toluene. However, I prefer to hold the amount of the alcohols which may be used to between 15 and 20% by weight of the total solvent. The dope may then be spread on the hereinbefore described flexible base, smoothed by a doctor blade, and the coat dried, preferably at an elevated temperature. Additional coats may be applied until the desired thickness is obtained. The softness of the various coats may be varied. The quantity of pigment may also be varied in the different coats. The smooth artificial leather may be embossed by the pressure of heated engraved plates or rollers to impart grain or other designs.

I will now describe a test which I have devised to show the relative differences in flexibility at low temperatures of various artificial leathers. This will be called the cold crack test and will be referred to in the examples to illustrate further the articles in accordance with this invention.

A strip of artificial leather $\frac{5}{8}$ " by 4" is hung in a closed chamber for 30 minutes in circulating air at a controlled temperature. The strip is then picked up by the ends with gloved hands and quickly and vigorously bent 180° over a $\frac{3}{8}$ " mandril rigidly mounted in the chamber, at the same time pulling the length of the strip over the mandril, the coated side being away from the mandril. The highest temperature at which the coating cracks is the temperature of failure.

Another test which I use to determine the quality of artificial leather measures the durability upon exposure to artificial sunlight, produced by a glass-enclosed cored-carbon arc in the device known as the "Fadeometer." A sample is exposed until the coating reaches a condition of embrittlement such that a vigorous 180° bend over a $\frac{3}{8}$ inch mandril causes the coating to crack at each of several places tested, the coated side being away from the mandril. The temperature is held at about 140° during exposure but the artificial leather is cooled for a half hour at room temperature before a bend test is made.

In the examples following, the artificial leather in accordance with my invention is illustrated by specific examples and its properties are further described by comparison with well known examples of prior art.

EXAMPLE I

A coating dope of the composition under Formula No. 1 of Table I 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

Table I

Formula	According to this invention		According to prior art	
	1	2	3	4
Dope composition:				
Nitrocellulose—12% nitrogen, 150 second viscosity	24	20	40	38
Ethyl cellulose—47.5% ethoxy, high viscosity	20	20	60	15
Raw castor oil	56			
Oxidized castor oil—“Baker's Pale No. 4”		60		62
Castor Oil	33	33	33	33
Titanium dioxide				
Solvent composition was:				
Ethyl acetate 15% by weight, butyl acetate 20% by weight, alcohol 15% by weight, toluene 50% by weight	370	340	330	320
Artificial leather properties:				
Temperature of failure in cold crack test.....°F.	-15	2	0	17
Minimum temperature causing exudation on heating 1 hour.....°F.	Above 195	Above 195	160	Above 195
Hours of exposure in the “Fadeometer” for embrittlement	162	220	116	162

the softener in the ratio of 70 parts pigment to 30 parts softener. All composition figures of these examples are in parts by weight. The coating dope obtained was then applied to cotton broken twill cloth weighing 9 ounces per square yard by the use of a doctor knife coater. Approximately twenty coats were applied, drying between coats, to obtain a coating with a dry weight of 9 ounces per square yard. The coated cloth was then embossed at 160° F. and 1500 pounds per square inch pressure for one minute to impart grain.

The superior properties of this artificial leather will be readily apparent upon a comparison with an artificial leather prepared in the same manner using the composition under Formula 3 of Table I. The properties are given under the respective formulas in Table I. The two products have identical softness at room temperature, say at 70° F. and are similar in pigmentation and in the flexible base. The article of Formula 3 has a flexibility in the cold equal to the best of prior art although its exudation temperatures are unsatisfactory in view of the requirements of the automobile industry, for example, of an exudation temperature above 175° F. to 180° F. Details of the cold crack and exposure tests have been hereinbefore discussed.

EXAMPLE II

The artificial leather of this example was prepared in the same manner as that of Example I except that a coating dope of the composition under Formula 2 of Table I was used. In this example the benefits of my invention are directed to extended durability without the heretofore usual loss of flexibility in the cold. The advance achieved is readily apparent by comparison with an artificial leather similarly prepared except using the composition under Formula 4 of Table I and it may be compared with the Formula 3 comparator of the previous example.

It will be understood that the details and ex-

amples given hereinbefore are illustrative only, and in no way limiting on my invention as broadly described hereinbefore and in the appended claims.

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

1. An artificial leather consisting of a flexible base web and thereon three to fourteen ounces per square yard of coating consisting essentially of layers of pigmented composition comprising nitrocellulose and ethyl cellulose soluble in organic solvents, with the ethyl cellulose between 10% and 80% of the two cellulose derivatives, and a softener essentially consisting of vegetable oil selected from the group consisting of castor oil, soya bean oil, oxidized castor oil, oxidized soya bean oil, oxidized cottonseed oil, partially polymerized castor oil, and mixtures thereof, said softener being compatible with the mixture of cellulose derivatives, the said composition layers being smooth, tough, homogeneous films deposited from organic solvent solutions in the absence of water and other immiscible liquids interfering with the film structure, the artificial leather being characterized by freedom from exudation of oil upon being heated, by improved flexibility at low temperatures in comparison with similar nitrocellulose artificial leather not containing ethyl cellulose, and by improved durability on exposure.

2. An artificial leather consisting of a flexible base web and thereon three to fourteen ounces per square yard of coating consisting essentially of layers of pigmented composition comprising nitrocellulose and ethyl cellulose soluble in organic solvents, with the ethyl cellulose between 10% and 80% of the two cellulose derivatives, and a softener consisting essentially of castor oil, the said composition layers being smooth, tough, homogeneous films deposited from organic solvent solutions in the absence of water and other immiscible liquids interfering with the film structure, the artificial leather being characterized by freedom from exudation of oil upon being heated, by improved flexibility at low temperatures in comparison with similar nitrocellulose artificial leather not containing ethyl cellulose, and by improved durability on exposure.

3. An artificial leather consisting of a flexible base web and thereon three to fourteen ounces per square yard of coating consisting essentially of layers of pigmented composition comprising nitrocellulose and ethyl cellulose soluble in organic solvents, with the ethyl cellulose between 10% and 80% of the two cellulose derivatives, and a softener consisting essentially of oxidized castor oil, the said composition layers being smooth, tough, homogeneous films deposited from organic solvent solutions in the absence of water and other immiscible liquids interfering with the film structure, the artificial leather being characterized by freedom from exudation of oil upon being heated, by improved flexibility at low temperatures in comparison with similar nitrocellulose artificial leather not containing ethyl cellulose, and by improved durability on exposure.

4. An artificial leather consisting of a flexible base web and thereon three to fourteen ounces per square yard of coating consisting essentially of layers of pigmented composition comprising nitrocellulose and ethyl cellulose soluble in organic solvents, with the ethyl cellulose between 10% and 80% of the two cellulose derivatives, and a softener consisting essentially of partially

polymerized castor oil, the said composition layers being smooth, tough, homogeneous films deposited from organic solvent solutions in the absence of water and other immiscible liquids interfering with the film structure, the artificial leather being characterized by freedom from exudation of oil upon being heated, by improved flexibility at low temperatures in comparison with similar nitrocellulose artificial leather not containing ethyl cellulose, and by improved durability on exposure.

5. An artificial leather consisting of a flexible base web and thereon three to fourteen ounces per square yard of coating consisting essentially of layers of pigmented composition comprising

nitrocellulose and ethyl cellulose soluble in organic solvents in approximately equal parts, and a castor oil softener compatible with the said mixture of cellulose derivatives, the said composition layers being smooth, tough, homogeneous films deposited from organic solvent solutions in the absence of water and other immiscible liquids interfering with the film structure, the artificial leather being characterized by freedom from exudation of oil upon being heated, by improved flexibility at low temperatures in comparison with similar nitrocellulose artificial leather not containing ethyl cellulose, and by improved durability on exposure.

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