

Sept. 19, 1939.

H. A. YOUNG

2,173,244

PROCESS FOR TREATING FIBROUS MATERIALS

Filed Jan. 3, 1938

2 Sheets-Sheet 1

Fig. 1.

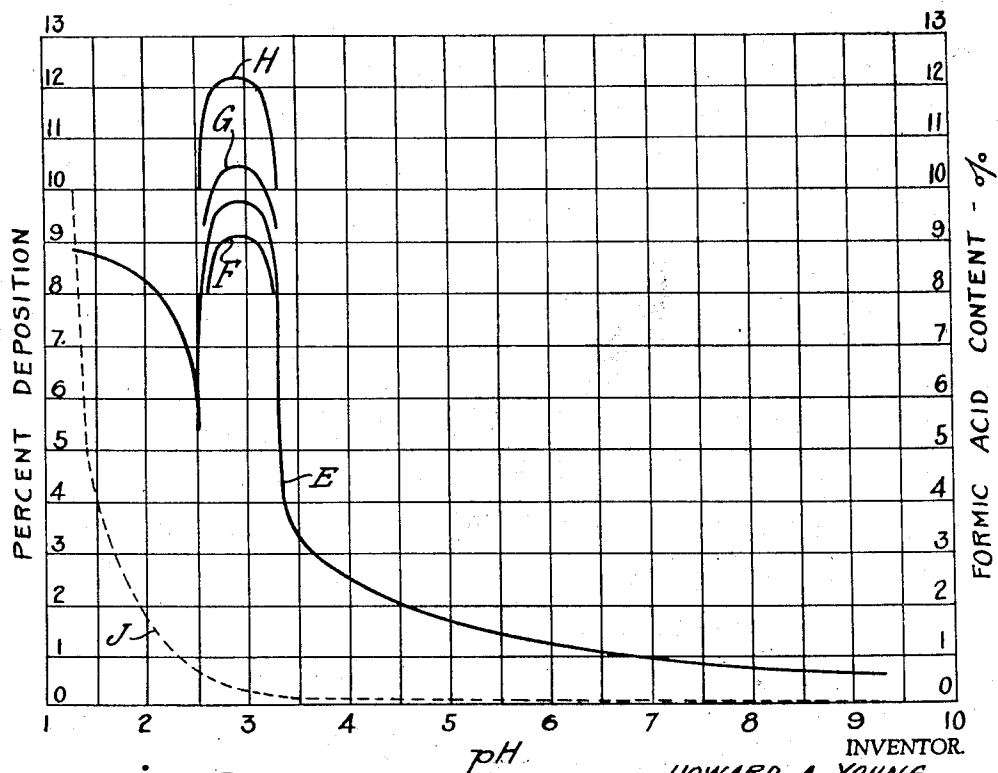
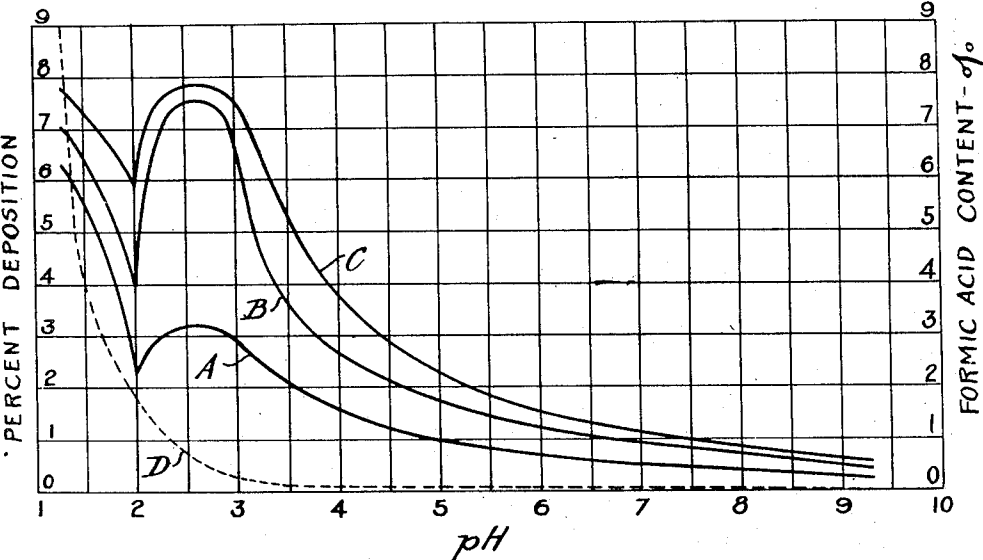


Fig. 2.

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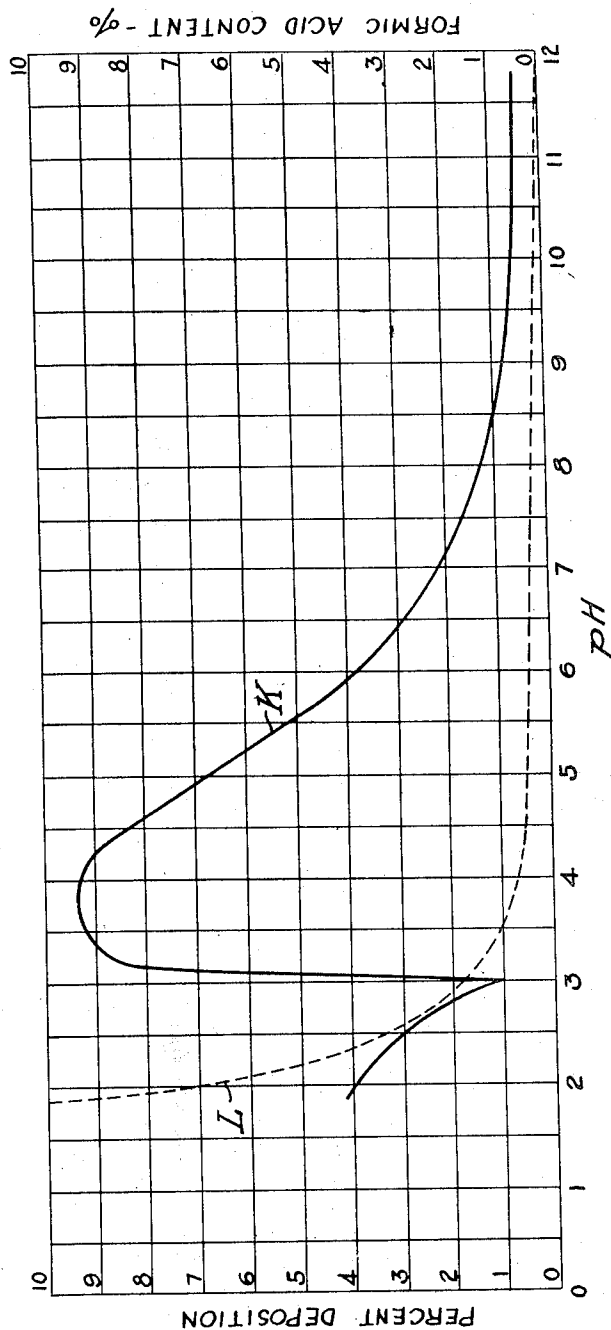
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2 Sheets-Sheet 2

Fig. 3.



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PROCESS FOR TREATING FIBROUS MATERIALS

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Application January 3, 1938, Serial No. 183,093

10 Claims. (Cl. 91-68)

This invention relates to a process for treating fibrous material and more particularly to a process for treating fibrous material with latex.

Various methods for treating fibrous materials with latex are known. Fibrous materials in the form of loose fibers or in the form of textile fabrics or other associations of fibers, have been introduced into a latex bath containing the desired amount of dispersed rubber and the fibrous material circulated with or through the bath or the bath circulated through the fibrous material until some or all of the dispersed rubber has been incorporated in the fibrous material. In these cases, the dispersed rubber has been deposited on the fibrous material by a coagulative deposition which may be effected by heating the bath with which the fibrous material has been treated in cases where the dispersed particles of rubber are coagulable by heat, or by the gradual addition of a coagulant or destabilizer to the bath, or by the previous treatment of the fibrous material with a coagulant for the dispersed rubber particles so that the fibrous material carries an excess of such coagulant, or by the previous preparation of a latex treating bath containing dispersed rubber particles having an electrical charge opposite in sign to that carried by the fibrous material so that the dispersed rubber particles become coagulated on the fibrous material by virtue of the neutralization of the particle charges.

According to the present invention, rubber is deposited on fibrous material by a non-coagulative deposition from a latex composition which is in its isoelectric zone. Dispersions of colloidal substance generally owe their stability, that is, their inability to settle out or coagulate, to the presence of electrical charges carried by the particles of the dispersed phase. Charged colloidal particles will migrate in an electrical field or towards an oppositely charged body. There is, however, as is well known, a region of hydrogen ion activity where the positive and negative charges on the dispersed particles are equal to each other and where the charges on the dispersed particles are neutralized. This region of electrical neutrality of the dispersed particles is called the isoelectric range or zone and the midpoint of this range is termed the isoelectric point. Dispersed particles having zero charge in their isoelectric zone will generally coagulate unless previously protected by an adequate amount of suitable stabilizer.

In carrying out the present invention, fibrous material is treated with a latex composition

which is at a pH in its isoelectric zone and which contains sufficient protective so that it is stable in the absence of the fibrous material, and the fibrous material is allowed to remain in contact with such an isoelectric latex composition, under normally non-coagulative conditions for the latex composition, that is, under conditions which would not produce coagulation of the latex composition itself were it not in contact with the fibrous material, until the desired amount of colloidal rubber particles have been deposited onto the fibers. Since the latex treating bath is stable and the conditions of treatment of the fibrous material with the treating bath would not coagulate the bath itself, and the latex composition is further isoelectric and hence contains no charged particles that will migrate to an electrically charged body, the deposition of the colloidal rubber particles on the fibrous material is a non-coagulative deposition. Such a non-coagulative deposition or union of the dispersed colloidal particles and the fibrous material is termed in this specification "sorption" and the capacity of a given fibrous material to "sorb" a colloidal material from a given dispersion is the "sorptive capacity" of such fibrous material. When rubber is deposited on fabrics from a latex composition in the isoelectric zone, the product retains to a great extent the "fabric feel" and appearance of untreated material. The latex treating bath may remain in contact with the fibrous material at room or at elevated temperature providing, of course, that the bath contains sufficient protective so that coagulation would not take place in the absence of the fibrous material under the time and temperature conditions of the treatment of the fibrous material with the latex composition. If it is desired to deposit all the rubber in a treating bath onto fibrous material with which the bath is associated in its isoelectric zone, the quantity of dispersed rubber in the treating bath should of course not be in excess of the sorptive capacity of the fibrous material for such rubber particles. The greater the amount of protective over the minimum necessary to stabilize the latex composition in the isoelectric zone in the absence of the fibrous material, the slower will be the rate of deposition of the rubber particles from the latex onto the fibrous material. I have discovered, however, that in all cases the rate of sorption of the colloidal rubber particles from the same treating bath onto the fibrous material is greater in the isoelectric zone than at a pH on either side of the isoelectric zone, regardless of whether the

rubber particles are given a positive or negative charge by so shifting the pH of the latex out of the isoelectric zone, and regardless of the sign of the charge on the fibrous material. This may readily be seen from the accompanying drawings in which:

Figure 1 is a chart showing the amount of rubber deposited from a vulcanized latex composition on silk hosiery in different periods of time at different pH's according to the procedure of Example 1;

Figure 2 shows the amount of rubber deposited in a given time on silk hosiery from different concentrations of the latex composition of Example 1 before vulcanization at various pH's according to Example 2; and

Figure 3 illustrates the amount of rubber deposited from a latex composition on woolen fabric in a given time at various pH's according to Example 3.

Various types of fibrous materials, such as woven, knitted, punched or felted fabrics, yarns, rovings, cords, skeins, and webs, such as water-laid felts from a paper making machine, or bats of fibers from a garnet or carding machine, or fiber slurries as in paper making, may be treated according to the present invention. Various fibers, as of wool, silk, cotton, viscose or acetate rayon, linen, cellulose and the like, or mixtures of the same, may be used, and these may be undyed, mordanted, dyed or otherwise treated so long as they are not in association with free coagulant which in the absence of the fiber would itself produce coagulation of the aqueous dispersion of colloidal material. Asbestos fibers can also be treated according to the present invention if the coagulants that are naturally associated with the fibers have been removed, or inactivated as by insolubilization.

In making up latex compositions according to the present invention, care should be taken to have sufficient protective present so that the isoelectric latex composition would not itself coagulate under the time and temperature conditions of the treatment with the fibrous material, if the latex were not in contact with the fibrous material, at the same time, too much protective should not be used or the rate of deposition of the rubber will be too slow due to the excess of protective, the bath will not exhaust, and deposition of the desired amount of rubber on the fibers will not satisfactorily take place. With a given latex compound and a given fibrous material, it is a very simple matter empirically to adjust the amount of the desired protective so that in the isoelectric zone the otherwise stable latex bath will readily deposit the required amount of rubber on the fibrous material in a given time. The term "latex" is used herein to designate broadly coagulable aqueous dispersions of elastic materials, including artificial dispersions of rubber or rubber-like materials, as well as natural latex, which may be preserved or compounded or otherwise treated as desired, as by vulcanization, and which may be in a normal, diluted, concentrated or purified condition produced by methods well known in the art.

A simple method may be used for determining the isoelectric range of a given latex compound, namely, by determining the migration or mobility of the dispersed rubber particles at different pH's under the influence of an electrical potential and noting the pH range of zero mobility or electrical neutrality. Other well known methods of determining the isoelectric point or

zone are based on the fact that at the isoelectric point the osmotic pressure, viscosity, and conductivity are at a minimum. In adjusting the pH of the latex in order to bring it into its isoelectric zone, the pH may be lowered where necessary by means of acids, such as formic, acetic, tartaric, phosphoric, hydrochloric, and sulphuric acids, as well as various acid salts, or mixtures of the same, or the pH may be raised, where necessary, by the addition of ammonia or other alkaline substance.

Two general classes of protectives may be used in preparing the latex treating composition, those of a colloidal nature and those of a non-colloidal nature. Different protectives may be used for preparing the dispersions of compounding ingredients for protecting the latex against coagulation on the addition of such compounding ingredients, and for stabilizing the latex treating bath in the isoelectric zone. Proteins, gums, soaps, vegetable mucilages, and starches are examples of colloidal protectives that may be used. Various known non-colloidal protectives may be used, such as certain salts of carboxyl ($R-COOH$), sulphonic ($R-SO_3H$), sulfinic ($R-SO_2H$), or phenolic ($R-OH$) groups or of ethereal sulphuric ($ROSO_3H$) radicals, where the R may have a straight chain or ring structure and may contain substituent halogen, amino, nitro or hydroxyl groups. Other organic chemicals are well known protectives as certain benzene sulphonic acids, their homologues and substitution products, naphthoic acids, aliphatic-aromatic acids, derivatives of hydro-aromatic series of acids, phenyl-glycine and derivatives.

In the case of the colloidal type of protective for dispersed particles in the latex composition, the protective becomes attached to the protected colloidal particles and the thus protected particles assume the charge and to some extent the properties and behavior of the colloidal protective agent and hence the isoelectric of the protective. It is believed that when a non-colloidal protective agent which is capable of ionizing is used to protect dispersed particles of rubber or protect colloidal compounding ingredients or compounding ingredients that have been peptized with a colloidal material, one of the ionized parts of the protective may fasten itself onto the colloidal material and in so doing may shift the isoelectric range of the dispersed material somewhat in proportion to the amount of protective added. When a colloidal protective agent is used and the dispersed particles assume the isoelectric of the colloidal protective, the deposition of the dispersed particles will be accompanied by a deposition of the colloidal protective and especially when an excess of colloidal protective over that merely necessary to stabilize the bath in the isoelectric zone is used. This may or may not be desirable. If it is objectionable for the colloidal protective to be deposited with the rubber or colloidal dispersed compounding ingredients, then a non-colloidal protective agent where possible should be used. Frequently both the colloidal and non-colloidal protectives may become modified by association with other ingredients of the latex compound, such as the dispersed rubber particles themselves or dispersed compounding ingredients or alkaline or acidic materials or salts which may be added for this purpose or because it is desired to include them in the latex composition, with the result that the complex associated colloids in the latex exhibit an isoelectric point different from

that of the protectives. However, it is always a simple matter to locate the isoelectric range in terms of hydrogen ion activity by means of cataphoretic tests, i. e., the conventional observations on colloid movement or migration under an impressed electrical force.

Various examples of the treatment of different fibrous materials with various latex compositions are set forth below, but these are merely exemplary of the invention and are not intended to be limitations thereof. The pH of the latex compounds in the following examples was lowered by means of formic acid because it is a volatile acid and has little effect upon the color and characteristics of fibrous materials, but other electrolytes as above described may be used satisfactorily for this purpose.

Example 1

In this case silk hose were treated by immersion in a treating bath made from latex compounded according to the following formula:

	Solids by weight
Rubber (as 60% centrifuged ammonia preserved latex)-----	100
"Aquarex D" (as 10% aqueous solution)---	1
Paste (as 25% colloid milled aqueous paste):	
"Aquarex D"-----	1
Colloidal sulphur-----	3
Zinc oxide-----	5
Zinc dimethyl dithiocarbamate-----	2
Piperidinium penta methylene dithiocarbamate-----	2
"Agerite White"-----	2
Glue-----	16
Gum arabic (as 10% aqueous solution)-----	10
Water to final total solids of 35%.	

The aqueous solution of "Aquarex D" was added to the centrifuged latex and to this was added the remaining materials in the form of a 25% paste, after which the whole was diluted with water to a final total solids of 35%. The "Aquarex D" is a stabilizer having the composition, monosodium sulphate ester of one-half lauryl and one-half myristal alcohol. The zinc dimethyl dithiocarbamate and the piperidinium pentamethylene dithiocarbamate are vulcanization accelerators. "Agerite White" is an antioxidant of the composition symmetrical di-beta-naphthyl-para-phenylene-diamine. The latex compound was vulcanized by a non-evaporative heating.

Various treating baths of the following composition containing amounts of formic acid ranging from 0 to 10% were made from the vulcanized latex compounded as above:

	Parts by weight
Solids of above latex compound-----	.6
"Aquarex D"-----	.2
Formic acid-----	0 to 10
Water-----	To make 100

Batches of silk stockings were immersed in about twenty times their weight of various treating baths at 95° F. containing formic acid in amounts from 0 to 10% of the bath, and agitated in the baths for various lengths of time, namely, 5, 10 and 15 minutes, before removing from the baths, rinsing and drying. The percent deposition of rubber on the fabrics under various pH condi-

tions of the treating baths in the 5, 10 and 15 minute periods were determined, and these results are shown in the chart of Fig. 1. Throughout the specification, the percent deposition of rubber on the fibrous material is calculated as percent gain based on the untreated fibrous material. The isoelectric zone of the treating bath extended from pH 2.25 to 2.95 and its midpoint at 2.60 was the isoelectric point as determined by cataphoretic tests. The amount of rubber deposited on the silk hose in the 5, 10 and 15 minute periods of treatment in the various treating baths which were in the pH range of 9.30 to 1.28, corresponding to formic acid contents of the bath ranging from 0 to 10%, are shown on the curves marked A, B and C respectively. The curve D shows the decrease in pH of the treating bath with increase of the formic acid content of the bath, and is typical of curves where the acid content is plotted against pH. The amount of formic acid added to the bath is considered the formic acid content of the bath. From each of the curves A, B and C it will be seen that the deposition of rubber is considerably greater in the isoelectric zone than on either side of it. The amount of rubber deposited at the isoelectric point in 5 minutes was about 3.1%, in 10 minutes about 7.5%, and in 15 minutes about 7.8%.

Raising the pH from the isoelectric zone results in the assumption of negative charges by the dispersed rubber particles and greatly reduces the amount of rubber deposited on the silk in a given time. Shifting the pH below the isoelectric range results in the assumption of positive charges by the dispersed rubber particles and at first likewise reduces the amount of rubber deposited on the silk in a given time. This reduction in the amount of dispersed rubber particles sorbed on the silk in a given time continues with a decrease in pH from the isoelectric point 2.60 to a pH of about 2.0, corresponding to an acid content of the bath of about 1.7%. On further reduction of the pH below 2.0, as to 1.28 by increasing the acid concentration from 1.7% to 10%, the amount of rubber deposited in a given time increases over the amount deposited at a pH of 2.0. When the acid content of the bath is increased over 1.7%, that is, when the pH is lowered below 2.0, the bath becomes destabilized and flocks and coagula appear in the bath. When the hose are immersed in such a bath below a pH of 2.0, visibly coarse particles of latex coagula are deposited on the silk. It is also obvious from the change in shape of the curve that a different mechanism is operating to deposit the rubber at pH's below 2.0 than at pH's above 2.0. That the treating bath when in the isoelectric zone is stable in the absence of fibrous material, may be shown by the fact that a treating bath in the isoelectric zone will leave no deposit on filtering through a No. 4 Watman filtering paper after a non-evaporative heating at 180° F. to 205° F. for 12 hours. Rubber particles sorbed on the silk hose in the isoelectric zone were not visible even under a four-power magnifying glass, the deposit being evenly distributed over the surface of the fiber. The "feel" of the stockings was scarcely different from that of untreated stockings and yet the run and wear resistance was greatly increased. The undesirable deposition of visibly coarse particles of latex coagula on the silk at pH's below 2.0 is believed to be the result of the chemical reaction of the excessive amounts of acid in these low pH ranges with the natural or added protectives on the latex

particles with the result that the protectives lose much of their protective power, and the consequent loss of stability of the latex permits the formation by coagulation of coarse particles of rubber which then attach themselves to the fibers when the hose are immersed in such a treating bath.

Example 2

In this case treating baths were made up from the latex compound of Example 1 but without heating to vulcanize the compound. Treating baths having a concentration of solids of the latex compound of .65% were made up with formic acid contents ranging from 0 to 10% according to the following formula:

	Parts by weight
Solids of above latex compound	.65
"Aquarex D"	2
Formic acid	0 to 10
Water	To make 100

The isoelectric zone of the treating bath extended from pH 2.65 to 3.25, and its midpoint at 2.95 was the isoelectric point as determined by cataphoretic tests. Other treating baths similar to the above were made with .2% "Aquarex D" and containing .50%, .80%, and .90% concentration of solids of the latex compound together with sufficient formic acid to give a number of pH's in the isoelectric range of 2.65 to 3.25 for these various concentrations of latex solids. Batches of silk hose were immersed in about 20 times their weight of the various treating baths at 95° F. and agitated in the baths for 10 minutes before removing from the baths, rinsing and drying. The percent rubber deposited on the silk hose in 10 minutes under various pH conditions at the different concentrations of the treating baths were determined, and these results are shown in the chart of Fig. 2. The amount of rubber deposited on the silk hose from the various treating baths containing .65% solids of the latex compound and which were in pH ranges of 9.30 to 1.28, corresponding to formic acid contents of the baths from 0 to 10%, are shown on the curve marked E. The amount of rubber deposited on the silk hose in 10 minutes in the various treating baths in the isoelectric range with concentrations of .50% to .80% and .90% of solids of the latex compound are shown on the curves marked F, G and H respectively. The curve J shows the decrease in pH of the latex treating bath with increase of the formic acid content of the bath and is the same as the corresponding curve D of Fig. 1. The curve E is similar in shape to curves A, B and C of Fig. 1 and curves F, G and H would be similar in shape if they had been extended to include deposition from baths at pH's throughout the range corresponding to 0 to 10% formic acid content of the bath instead of being restricted to points in and adjacent to the isoelectric zone.

A comparison of curves E, F, G and H shows, as would be expected, that the isoelectric zone is dependent on the pH and not the concentration of solids in the latex treating bath. A comparison of these curves further shows an increase in rubber deposited in the isoelectric zone with an increase in concentration of dispersed rubber particles. This, of course, would be typical of cases where the bath was not exhausted at the lower concentrations in a given time or the amount of deposit from the bath of lower concentration was not equal to the sorptive capacity of the fibrous material in the time in which de-

posits at various concentrations were being compared. A comparison of the curves of Fig. 2 and Fig. 1 shows a greater deposit from unvulcanized latex than from a similar vulcanized latex under the same condition of treatment. A further comparison of Fig. 2 and Fig. 1 shows that vulcanization of the latex compound used in preparing the treating baths causes a lowering of the isoelectric point, namely, from 2.95 to 2.60, and a somewhat flattening out of the peaks of the deposition curves. The amount of rubber deposited in 10 minutes at the isoelectric point from a treating bath having a concentration of the solids of the latex compound of .50% was about 9.1%; a similar deposit from a bath having a solids content of 6.5% was about 9.8%; the deposit from a bath having a solids content of .80% was about 10.4% and the deposit from a bath having a solids content of .90% was about 12.1%. With the various treating baths having a concentration of .65% there was an increase in the amount of rubber deposited as the pH's were lowered from 2.0, as to 1.28 corresponding to an increase in the acid content from .6 to 10%. This is similar to the increase in deposit in Example 1 at pH's below 2 corresponding to increasing the acid content in that case above 1.7, as may be seen from the curves of Fig. 1. As in Example 1, these depositions below a pH of 2.0 were from unstable latices and produced visibly coarse particles of latex coagula on the silk hose.

Example 3

In this case rubber was deposited on a wool flannel fabric from a treating bath made from a latex compound of the following formula:

	Solids by weight
Rubber (as 60% centrifuged ammonia preserved latex)	100
Potassium hydroxide (as 25% aqueous solution)	2
Glue (as 25% aqueous solution)	.4
"Aquarex D" (as 10% aqueous solution)	1.25
Paste (as 35% aqueous paste):	
Mercaptobenzothiazol	.5
Dimethylammonium dimethyl dithiocarbamate	.5
Solubilized casein	4
Colloidal sulphur	2
Zinc oxide	2.5
"BLE"	.5
Water to final total solids of 40%	

The aqueous solutions of potassium hydroxide, glue and "Aquarex D" were added to the centrifuged latex and to this was added the remaining materials in the form of a 35% aqueous paste, after which the whole was diluted with water to a final total solids of 40%. The casein in the paste was solubilized by means of a small amount of borax and sodium fluoride in a manner well known in the art. The mercaptobenzothiazol and dimethylammonium dimethyl dithiocarbamate are vulcanization accelerators. "BLE" is the trade name of an antioxidant which is a condensation product of acetone and diphenylamine. Various treating baths of the following composition containing amounts of formic acid ranging from 0 to 10% were made from the above latex compound:

	Parts by weight
Solids of above latex compound	10
"Emulphor O"	1
Formic acid	0 to 10
Water	To make 100

"Emulphor O" is the trade name of the commercial stabilizer which was used to stabilize the treating bath and is a condensation product of ethylene oxide and higher alcohols. The treating bath in this case was of much higher concentration than those used in the previous examples and was used in a padding procedure. Various treating baths containing formic acid in amounts from 0 to 10% were padded onto pieces of woolen flannel fabric by passing the fabric pieces through the treating baths and squeezing through rollers so that the fabric pieces contained about 100% of their weight of the treating baths, that is, a weight of liquid bath in the fabric about equal to the weight of the fabric, or a so-called "bath-to-goods" ratio of 1:1. These pieces of fabric treated with the various baths were allowed to rest at 70° F. for 60 minutes, after which they were rinsed and dried. The percent rubber deposited on the fabrics under the various pH conditions of the treating baths were determined and these results are shown in the chart of Fig. 3. The isoelectric zone of the treating bath extended from pH 3.25 to 4.25 and its midpoint at pH 3.75 was the isoelectric point as determined by cataphoretic tests. The amount of rubber deposited on the fabric in the various treating baths which were in the pH range of 11.85 to 1.85, corresponding to formic acid contents of the baths ranging from 0 to 10%, are shown on the curve marked K. The curve L shows the decrease in pH of the treating bath with increase of the formic acid content of the bath. The curve K although illustrating deposition from a relatively high concentration by a padding procedure, shows the same behavior as the curves of Figs. 1 and 2 showing deposition from relatively dilute treating baths by immersion procedures. From curve K it will be seen that the deposition of rubber is considerably greater in the isoelectric zone than on either side of it. With the treating baths in the isoelectric zone, there was substantially complete exhaustion of the baths.

Raising the pH from the isoelectric zone results in the assumption of negative charges by the dispersed rubber particles and greatly reduces the amount of deposit of rubber on the fabric in a given time. Shifting the pH below the isoelectric range results in the assumption of positive charges by the dispersed particles and at first likewise reduces the amount of rubber deposited on the fabric in a given time similarly to the curves in Figs. 1 and 2. This reduction in the amount of rubber particles sorbed on the fabric in a given time continues with decrease in pH from the isoelectric point down to a pH of about 3.0, corresponding to an acid content of a bath of about 1.6%. On further reduction of the pH below 3.0; as to 1.85 by increasing the acid concentration from 1.6% to 10%, the amount of rubber deposited in a given time increases over the amount deposited at a pH of 3.0 showing the same behavior as in the examples of Figs. 1 and 2. When the acid content of the bath is increased over 1.6%, that is, when the pH is lowered below 3.0, the bath becomes destabilized and flocks and coagula appear in the bath. When the fabrics are treated with such a bath below a pH of 3.0, visibly coarse particles of latex coagula are deposited on the fabric. As in examples of Figs. 1 and 2, it is obvious from the change of the shape of the curve that a different mechanism is operating to deposit the rubber at pH's below 3.0 than at pH's above 3.0.

Curves similar to those of Figs. 1, 2 and 3 may

be obtained from the deposition of rubber from various other latex treating baths on various types of fibrous materials and such curves will all show that the sorptive deposition of the rubber particles is a maximum when the treating bath is in the isoelectric zone. In the remaining examples, however, it will be sufficient to illustrate the deposition of rubber from variously compounded latex treating baths upon various fibrous materials at a single pH in the isoelectric zone of the treating bath, and in some cases to compare such isoelectric deposition with a deposition under similar conditions at a pH outside the isoelectric range.

Example 4

In this case the latex compound of Example 3 was made up into a more dilute treating bath than in Example 3 for deposition of rubber by immersion procedures on various woolen fabrics. The latex compound of Example 3 was diluted with water and acidified to a pH in the isoelectric zone according to the following formula:

Parts by weight	
Solids of latex compound of Example 3	.9
"Aquarex D"	.2
Formic acid	4.8
Water	94.1

The pH of the bath which was in the isoelectric zone, as shown by cataphoretic tests, was 1.73. A woolen "boucle" fabric was immersed in about 20 times its weight of this bath and agitated for 10 minutes at 80° F. and then rinsed and dried. It showed a gain of weight of 16.3% or about 90% exhaustion of the bath. A woolen flannel fabric similarly treated for 20 minutes at 65° F. showed a weight gain of 14% or about 78% exhaustion of the bath. Woolen serge khaki uniform material similarly treated for 15 minutes at 100° F. showed a weight gain of 11.3% or about 63% exhaustion of the bath. Woolen automobile upholstery similarly treated for 15 minutes at 83° F. showed a weight gain of 12.7% or about 71% exhaustion of the bath. Khaki whipcord material similarly treated for 15 minutes at 95° F. showed a weight gain of 12.7% or about 71% exhaustion of the bath. A blue worsted suiting material similarly treated for 10 minutes at 100° F. showed a 12.2% weight gain or about 68% exhaustion of the bath. A 50% wool and 50% cotton automobile upholstery fabric similarly treated for 9 minutes at 95° F. showed a weight gain of 15.8% or about 88% exhaustion of the bath.

Other treating baths made from the latex compound of Example 3 with various protectives for the treating bath and as applied to various types of fibrous material are shown in Examples 5 to 7.

Example 5

The treating bath had the following composition:

Parts by weight	
Solids of the latex compound of Example 3	.6
"Lauryl super sulphate-N"	.35
Formic acid	.65
Water	98.4

Woolen flannel fabric was immersed in about 20 times its weight of the treating bath and after agitating for 15 minutes at room temperature, the bath had cleared showing exhaustion of the bath and the fabric after rinsing and drying showed a gain of 13.2%. The pH of the bath which was isoelectric was 2.3. "Lauryl

super sulphate-N" is the trade-name for a stabilizer which is a hydrogenated oil which is sulphonated.

Example 6

- 5 The composition of the treating bath was as follows:

	Parts by weight
Solids of the latex compound of Example 3	10.
"Vultamol"-----	1.5
10 Formic acid-----	2.7
Water-----	85.8

- The above treated composition was padded onto a woolen automobile fabric by running the fabric through the bath and squeezing out the excess bath between squeeze rolls in a manner to leave about 150% entrainment, that is, a weight of treating bath held in the fabric equal to about one and one-half times the weight of the fabric, or a bath-to-goods ratio of 1.5:1. The pH of the treating composition which was isoelectric was 2.1. The fabric with the liquid held in it was allowed to rest 20 minutes at room temperature, and then washed and dried. The rinse was clear, showing exhaustion of the treating bath, and the gain in weight was 14.6%. "Vultamol" which is sold by the General Dyestuff Corp., is the trade name of a stabilizer whose composition is not known but which is believed to be a sulphated oil.

Example 7

- The composition of the treating bath was as follows:

	Parts by weight
35 Solids of latex compound of Example 3-----	10
"Aquarex D"-----	1
Formic acid-----	4.8
Water-----	84.2

- 40 The fabric was a stock dyed automobile fabric, 56" wide and 22 oz. in weight per linear yard. It had an all wool warp and a 30% cotton and 70% wool filling, the warp weight being half the fabric weight. A 60 yard piece of the fabric was run through the treating bath in the flat, wrung in the flat to avoid surface marking and to get uniform distribution of the treating bath, to about 100% entrainment, or a bath-to-goods ratio of 1:1, and allowed to rest at room temperature for 15 minutes. The fabric was then rinsed and dried. The rinse was clear showing exhaustion of the entrainment. The pH of the bath which was isoelectric was 1.73. The gain in weight was 10%, with a gain in tensile strength of 20%, and an increase in resistance to abrasion of 500%.

Example 8

- The latex compound for use in preparing the treating bath in this case was made up as follows:

	Solids by weight
Rubber (as 60% centrifuged ammonia preserved latex)-----	100.
60 "Aquarex D" (as 10% aqueous solution)-----	1
65 Paste (as 35% colloid milled aqueous paste):	
"Aquarex D"-----	1
Colloidal sulphur-----	3
Zinc oxide-----	5
70 Zinc dimethyl dithiocarbamate-----	2
Piperidinium pentamethylene dithiocarbamate-----	2
Glue-----	.63
Gelatin-----	5
75 Water to final total solids of 35%	

The aqueous solution of "Aquarex D" was added to the centrifuged latex and to this was added the remaining materials in the form of a 35% aqueous paste, after which the whole was diluted with water to a final total solids of 35%.

Wool flock was treated with about twenty times its weight of a treating bath made up from the above latex compound and having the following formula:

	Parts by weight
Solids of above latex compound-----	.9
"Aquarex D"-----	.2
Formic acid-----	3.4
Water-----	95.5

The "Aquarex D" dissolved in 46 parts of the water was just added to the flock, rapidly wetting the flock. The latex compound with an additional 38 parts of water was then added and finally the 3.4 parts of formic acid with the remaining 10 parts of water. After addition of the formic acid and agitation of the flock for ten minutes at room temperature, the bath exhausted and the flock was filtered, washed and dried. The flock showed a gain of 18%. The pH of the bath which was isoelectric after the addition of the formic acid was 1.95. Until the addition of the formic acid to bring the bath into the isoelectric zone, no rubber deposited from the bath onto the flock.

The application of the present invention to various artificial dispersions of rubber is illustrated in the following examples:

Example 9

In this case the treating bath was made from an artificial dispersion of reclaim rubber. The formula for the dispersion was as follows:

	Solids by weight
Tube reclaim-----	100.
Rosin-----	6
Sodium hydroxide-----	.75
Water to final total solids of 50%	

The dispersion was made up in the usual manner by mixing the rosin and said hydroxide dispersing materials into the reclaimed rubber after plasticizing, and adding water until an inversion of phase, whereupon the rubber became dispersed in the water, and adding further water to dilute to 50% solids content.

The treating bath made from the above dispersion had the following composition:

	Parts by weight
Solids of above dispersion compound-----	.5
"Aquarex D"-----	.15
Formic acid-----	5
Water-----	94.35

Woolen fabric was immersed in about 20 times its weight of the treating bath at 80° F. and agitated for 10 minutes, rinsed and dried. The fabric showed a gain of 11% weight with exhaustion of the bath. Under the same conditions but without addition of the formic acid to the treating bath, the fabric showed only a 4.3% weight gain. The pH of the bath which was in the isoelectric zone was 1.25.

Example 10

In this case the treating bath was made from

an artificial dispersion of crude rubber of the following formula:

	Solids by weight
Smoked sheet-----	100
Rosin -----	12
Sodium hydroxide-----	1.56
Water to final total solids at 50%	

The dispersion was made up as in the previous case by mixing the rosin and sodium hydroxide dispersing materials into the crude rubber after plasticizing, and adding water until an inversion of phase and dilution to 50% total solids content.

The treating bath which in this case was for an entrainment procedure, had the following composition:

	Parts by weight
Solids from above dispersion compound-----	10
"Gardinol WA"-----	2
Formic acid-----	7.5
Water-----	80.5

Woolen fabric was passed through the treating bath and squeezed between squeeze rolls to an entrainment of about 100%. The fabric was permitted to rest for 20 minutes at room temperature, washed and dried. The rinse was clear showing exhaustion of the entrainment. The gain in weight was 11%. The pH of the bath which was isoelectric was 1.2. Gardinol WA is the trade name of a stabilizer which is the sodium salt of sulphated lauryl alcohol.

The above examples clearly illustrate the present invention and it will be obvious to those skilled in the art that various other treating baths than those illustrated in the above examples may be developed for the treatment of various fibrous materials using the principles of the present invention. In view of the many changes and modifications that may be made without departing from the principles underlying the invention, reference should be made to the appended claims for an understanding of the invention.

This application is a continuation-in-part of application Serial No. 149,270, filed June 19, 1937.

Having thus described my invention, what I claim and desire to protect by Letters Patent is:

1. The process of treating fibrous material which comprises associating a latex composition which is stable and at a pH in approximately its isoelectric zone with fibrous material under normally non-coagulative conditions for the latex composition, said latex composition being stable in the absence of fibrous material but capable of depositing substantially all of its rubber particles on fibrous material under normally non-coagulative conditions for the latex composition, and maintaining the fibrous material associated with said bath under normally non-coagulative conditions for the latex composition until the desired amount of rubber has been sorbed on the fibrous material.

2. The process of treating fibrous material which comprises associating a latex composition which is stable and at a pH in approximately its isoelectric zone with fibrous material under normally non-coagulative conditions for the latex composition, said latex composition containing sufficient protective to stabilize it in the isoelectric zone in the absence of fibrous material but insufficient protective to prevent substantially all the dispersed rubber particles from being capable of depositing on fibrous material under normally

non-coagulative conditions for the latex composition, and maintaining the fibrous material associated with said bath under normally non-coagulative conditions for the latex composition until the desired amount of rubber has been sorbed on the fibrous material.

3. The process of treating fibrous material which comprises associating a bath of a latex composition which is at a pH in approximately its isoelectric zone with fibrous material under normally non-coagulative conditions for the latex composition, said latex composition containing an acid and sufficient protective to stabilize it in the isoelectric zone in the absence of fibrous material but insufficient protective to prevent substantially all the dispersed rubber particles from being capable of depositing on fibrous material under normally non-coagulative conditions for the latex composition, and maintaining the fibrous material associated with said bath under normally non-coagulative conditions for the latex composition until the desired amount of rubber has been deposited on the fibrous material.

4. The process of treating fibrous material which comprises associating a bath of a latex composition which is at a pH in approximately its isoelectric zone with fibrous material under normally non-coagulative conditions for the latex composition, said latex composition containing an acid and sufficient protective to stabilize it at elevated temperature in the isoelectric zone in the absence of fibrous material but insufficient protective to prevent substantially all the dispersed rubber particles from being capable of depositing on fibrous material at elevated temperature under normally non-coagulative conditions for the latex composition, and maintaining said fibrous material associated with said bath under normally non-coagulative conditions for the latex composition until the desired amount of rubber has been deposited on the fibrous material.

5. The process of treating fibrous material which comprises associating with fibrous material a bath of a latex composition which is at a pH in approximately its isoelectric zone, said bath containing sufficient protective so that it is stable in its isoelectric zone in the absence of the fibrous material but containing insufficient protective to prevent substantially all the dispersed rubber particles in the bath from being capable of depositing on the fibrous material under normally non-coagulative conditions for said latex composition, and maintaining said fibrous material associated with said bath under normally non-coagulative conditions for said latex composition until at least part of the rubber has been sorbed on the fibrous material.

6. The process of treating fibrous material which comprises associating with fibrous material a bath of a latex composition which is at a pH in approximately its isoelectric zone, said bath containing sufficient protective so that it is stable in its isoelectric zone in the absence of the fibrous material but containing insufficient protective to prevent substantially all the dispersed rubber particles in the bath from being capable of depositing on the fibrous material under normally non-coagulative conditions for said latex composition, and maintaining said fibrous material associated with said bath under normally non-coagulative conditions for said latex composition until substantially all the rubber in the latex composition has been sorbed on the fibrous material.

7. The process of treating fibrous material which comprises associating with fibrous material at room temperature a bath of a latex composition which is at a pH in approximately its isoelectric zone, said bath containing sufficient protective so that it is stable in its isoelectric zone in the absence of the fibrous material but containing insufficient protective to prevent substantially all the dispersed rubber particles in the bath from being capable of depositing on the fibrous material in the absence of free coagulant on the fibrous material, and maintaining the bath associated with the fibrous material at room temperature and in the absence of free coagulant on the fibrous material until at least part of the rubber has been sorbed on the fibrous material.

8. The process of treating fibrous material which comprises associating with fibrous material at room temperature a bath of a latex composition which is at a pH in approximately its isoelectric zone, said bath containing sufficient protective so that it is stable in its isoelectric zone in the absence of the fibrous material but containing insufficient protective to prevent substantially all the dispersed rubber particles in the bath from being capable of depositing on the fibrous material in the absence of free coagulant on the fibrous material, and maintaining the bath associated with the fibrous material at room temperature and in the absence of free coagulant on the fibrous material until substantially all the rubber in the latex composition has been sorbed on the fibrous material.

9. The process of treating fibrous material which comprises associating with fibrous mate-

rial at elevated temperature a bath of a latex composition which is at a pH in approximately its isoelectric zone, said bath containing sufficient protective so that it is stable in its isoelectric zone in the absence of the fibrous material at elevated temperature but containing insufficient protective to prevent substantially all the dispersed rubber particles in the bath from being capable of depositing on the fibrous material in the absence of free coagulant on the fibrous material, and maintaining the bath associated with the fibrous material at elevated temperature and in the absence of free coagulant on the fibrous material until at least part of the rubber has been sorbed on the fibrous material.

10. The process of treating fibrous material which comprises associating with fibrous material at elevated temperature a bath of a latex composition which is at a pH in approximately its isoelectric zone, said bath containing sufficient protective so that it is stable in its isoelectric zone in the absence of the fibrous material at elevated temperature but containing insufficient protective to prevent substantially all the dispersed rubber particles in the bath from being capable of depositing on the fibrous material in the absence of free coagulant on the fibrous material, and maintaining the bath associated with the fibrous material at elevated temperature and in the absence of free coagulant on the fibrous material until substantially all the rubber in the latex composition has been sorbed on the fibrous material.

HOWARD A. YOUNG.