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# PROCESS FOR MAKING A UNIFIED FIBROUS WEB

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This invention relates to a normally tacky and pressure-sensitive adhesive sheet and, more particularly, to a normally tacky and pressure-sensitive adhesive sheet comprising a paper backing having improved wet tensile strength and delamination resistance.

Paper-backed normally tacky and pressure-sensitive adhesive tapes require internal strengthening of the paper-backing element in order to prevent delamination thereof upon unrolling the tape or upon removal from the surface to which it is applied. Generally, elastomeric (i.e. rubbery) polymers are incorporated in the paper sheet in order to strengthen them to the required degree. Various procedures have been developed for incorporating the polymer in the sheet including dispersion of the polymeric materials in organic solvents and impregnation with such a solution, impregnation with an aqueous latex of such elastomeric polymers, and incorporation of the polymer onto the fibers with subsequent formation of a sheet including the fibers and rubbery bonding particles.

The latter procedure has definite advantages in ease of processing, control of fiber and bonding particle distribution, tensile strength both in the machine direction and across the sheet, etc. It has been found, however, that with the use of such a procedure, the resistance to delamination of the paper web is of a somewhat lower order of magnitude compared to a sheet prepared by saturation of a formed web with such rubbery polymers. Additionally, the wet strength properties of webs, including such elastomeric bonding particles, regardless of how formed are not all to be desired.

Accordingly, it is an object of this invention to provide a method of unifying a fibrous web for use as a backing element for a pressure-sensitive adhesive sheet wherein the elastomeric polymers are incorporated in the web by a beater-impregnation procedure but increased wet tensile strength and delamination resistance are obtained.

It is an additional object of the invention to provide a simple and rapid procedure for obtaining a beater-impregnated paper backing of improved characteristics.

It is a further and more specific object of this invention to provide a normally tacky and pressure-sensitive adhesive tape formed with a paper backing of improved characteristics so far as wet tensile strength and delamination resistance is concerned.

These and other objects of the invention will become apparent when reference is made to the detailed description appearing hereinafter. It is to be appreciated that the details given are exemplary and the invention is not to be considered limited thereto.

In its broadest aspect this invention comprises a process for the improvement in the unification of a felted fibrous web made by the deposition of an elastomeric polymer onto the fibers prior to sheet formation with the subsequent treatment of the formed sheet with a resinous polymer incompatible with the elastomeric polymer present in the sheet. It has been found that a greater degree of unification can be obtained by the incorporation of two or more incompatible polymers into the sheet



by such a procedure than can be obtained by the use of one polymer or a combination of compatible polymers at comparable levels of treatment. The advantages of the invention are particularly obtained when applied to sheets comprising rubbery polymers and fibers where the principal dependence for sheet unification is placed on the rubbery polymer. In addition to the use of such sheets as backings for pressure-sensitive adhesive tapes, they may be used for bookbinding stock, shoe midsoles, shoe cover stock, and the like. In addition to the described benefits, additional advantages of good flexibility of the sheet and a reduction in the amount of bonding material required for a given level of unification are obtained.

In accordance with the invention and as an initial step therein, fibers of the type conventionally used to form papers for use in paper-backed normally tacky and pressure-sensitive adhesive tapes are slurried to form a conventional pulp slurry. Preferably, the fibers are kraft pulp, semi-bleached, but any conventional paper fiber of the type indicated may be employed.

An elastomeric polymer of the type conventionally employed in unifying beater-impregnated fibrous webs is also dispersed in the slurry, conventionally in the beater. Such elastomeric polymers may comprise conventional rubbery polymers and copolymers such as those of butadiene-acrylonitrile, butadiene-styrene, natural rubber, butyl rubber, polychloroprene, vinyl chlorides, alkyl acrylates, etc. For ease of processing, such elastomeric polymers are incorporated into the slurry of fibers in the form of an aqueous latex of the polymer.

The polymer is then precipitated on the fiber in any suitable manner. Preferably the polymer is precipitated on the fiber by the use of a water-soluble polymer having at least three functional groups capable of substantial ionization in water to furnish ions of a particular charge to the aqueous system. The precipitating polymers preferably used are of the type disclosed in the previous application in which the inventor was an applicant, United States application Serial No. 210,282, filed February 9, 1951. As indicated in that application, such polymers include: (1) the reaction product of a guanidine salt with an aldehyde under basic conditions, as described in said application, (2) salts of water soluble quaternary ammonium resulting from the reaction of a primary diamine such as propylene diamine, an alkyl halide such as 1-, 4-dichlorbutane, and a halogenated alkyl compound such as butyl bromide, reacted under conditions unfavorable to ring formation, (3) salts of polyvinylamine, such as the acetate, (4) salts of polyethylene imine, such as the acetate or sulfate, (5) salts of long chain polymeric secondary amines such as are formed by the reaction of 1-, 4-dibromobutane and 1-6 hexamethylene diamine, and (6) salts such as the chloride or acetate of mixed primary and secondary amines.

After precipitation of the elastomeric polymers on the fiber to the desired degree, the sheet is formed by a conventional paper-making operation using, for example, a Fourdrinier or cylinder machine.

After the sheet is formed, and preferably after drying the sheet to a stage where most of the water remaining after drainage and suction on the paper machine is removed, it is then treated with a solution of a resinous polymer incompatible with the elastomeric polymer in the sheet and obtained by the reaction of an aldehyde, preferably formaldehyde with urea, melamine, or phenol or a mixture thereof. The resin employed is of the type conventionally employed in imparting wet strength to paper and, if desired, the resin, particularly the urea or melamine resin, may be modified in conventional manner by condensation in the presence of an amine. The resin

solution, preferably aqueous, may be applied to the formed sheet in any suitable manner as by roller application, a doctor blade, etc. As heretofore indicated, the resin is applied after the sheet has almost dried, and the application may take place at a stage incorporated into the paper machine, for example, after series of drying drums, and be followed by drying on the paper machine or in a suitable drying oven.

The ratio of the resinous polymer added to the sheet to the elastomeric polymer deposited in the sheet before formation may be varied widely. Preferably, the components are in the sheet in amount about 10 to 100 parts by weight of elastomeric polymer and about ½ to 5 parts by weight of resinous polymer based on 100 parts by weight of fiber. Normally, the ratio of fiber to elastomeric polymer to resinous polymer will be approximately 100:20:1 all by weight. Such a ratio has been found to be most advantageous in obtaining a desired balancing of characteristics of the web. Generally, if the rubbery polymer content is too high, some difficulty in incorporating the resinous polymer in the formed sheet may occur. On the other hand, undesirable qualities such as stiffness may be apparent if the level of treatment with the resinous polymer is high with respect to the amount of elastomeric polymer in the sheet. Too little resinous polymer with respect to the rubbery polymer results in a gradual diminishing of effect as would be expected.

The following are examples of fibrous webs unified in accordance with this invention as compared to fibrous webs unified by prior methods. It is to be appreciated that the compounds and proportions listed are exemplary and the invention is not to be considered limited thereto.

## EXAMPLE I

Two sheets of paper were formed by the following procedure:

Kraft pulp (semi-bleached) was beaten to 260 cc. Canadian Standard Freeness and 20% by weight of the pulp of a synthetic rubber, a copolymer of 75% acrylonitrile, 25% butadiene by weight with a Mooney plasticity of about 55, was precipitated onto the pulp fibers in the beater by means of the polymeric guanidine carbonate-formaldehyde precipitating agent disclosed in U.S. application Serial No. 210,281. Freeness of the stock after precipitation of the rubber was 520 cc. Canadian Standard. The stock was Jordaned before going on the paper machine to a freeness of 270 cc. Canadian Standard. After formation the sheet weight was 70 pounds (24 x 36×480) and the dry sheet had a tensile strength in the machine direction approximately three times that of the cross machine tensile.

One sample of the paper thus formed was given a size press treatment with a 3% solids solution of a urea formaldehyde resin modified by condensation of the urea and formaldehyde in the presence of an amine. The resin solution had a pH of 6.5 and sheet pickup was 35.3% of the solution, resulting in a resin content of the finished sheet of 1.06% by weight. Physical test results on the sheet treated in accordance with this invention and including the resinous polymer and the sheet formed without treatment with the resinous polymer were as follows:

*Table I*

| | Dry M. tensile, lbs./in. width | Wet tensile, lbs./in. width | Delamination resistance, oz./in. width |
|---|---|---|---|
| Sheet with urea resin | 47.6 | 20 | 21 |
| Sheet without urea resin | 41.5 | 6.3 | 17 |

NOTE.—Force in ounces per inch width necessary to separate test strip into two plies.

The foregoing data clearly indicate the decided improvement in tensile strength, wet and dry, and in the delamination resistance obtained in the sheet treated in accordance with this invention as compared to the sheet formed without treatment with the incompatible resinous polymer. In addition to the advantages shown by the data, it was noted that the sheet formed in accordance with the invention exhibited a substantially greater flexibility than the control, a very important characteristic in those instances where the unified sheet is to be used as a backing for a normally tacky and pressure-sensitive adhesive tape.

## EXAMPLE II

Results similar to those obtained in Example I may be obtained by the use of a melamine-aldehyde resin in place of the urea-aldehyde resin indicated. For example, sheets were formed by substantially the same procedure as listed in Example I except for the use of a copolymer of 50% by weight butadiene and 50% styrene with a Mooney value of about 70 deposited in the sheet in amount about 22½% by weight of the pulp. One sample was thereafter treated with a commercial melamine resin of the type described in U.S. Patent No. 2,345,543. The melamine resin was prepared by dissolving a commercial melamine-aldehyde condensation product comprising largely methylol melamines in hydrochloric acid solution to form an "acid type" resin solution which was aged overnight as described in the aforementioned patent. A pickup of about 1% melamine resin was obtained.

The sample thus treated exhibited a delamination resistance of about 22 ounces/inch width compared with about 17 ounces/inch width for the sample which contained no resin. Additionally the sheets exhibited better tensile strength both wet and dry, and better flexibility than the control sample.

Sheets unified in accordance with this invention may be employed as backing elements for normally tacky and pressure-sensitive adhesive tapes by coating the sheet on at least one surface with any conventional normally tacky and pressure-sensitive adhesive. An adhesive formed of:

| | Parts weight |
|---|---|
| Crude rubber | 100 |
| Rosin, dehydrogenated | 90 |
| Aluminum hydrate | 90 |
| Mineral oil | 30 |
| Antioxidant | 2 |

and coated on the sheet in amount approximately 2 ounces per square yard coated, may be advantageously employed. If it is desirable, conventional backsizing compositions and release agents may be applied to the surface of the paper backing opposite that to which the adhesive is coated.

When so formed, adhesive tapes employing the backing of this invention exhibit characteristics of high internal strength enabling unrolling thereof and removal from the surface to which they are applied without delamination, excellent flexibility enabling good conformance to the surface to which they are applied, and good wet and dry tensile strength.

It will be appreciated that many variations in the invention described herein may become apparent to those skilled in the art to which this invention applies. It is to be appreciated that such variations are within the concept of the invention described herein.

What is claimed is:

1. The method of preparing a unified cellulosic fibrous web having improved wet tensile strength and delamination resistance which comprises forming an aqueous slurry of fibers, incorporating an elastomeric polymer into said slurry, precipitating said elastomeric polymer on said fibers by adding to said slurry a water-soluble polymer having at least three functional groups capable of substantial ionization in water, sheeting the fibers and pre-

cipitated elastomeric polymer to form a bonded fibrous web thereof, and then incorporating into said formed web a resinous polymer incompatible with said elastomeric polymer, said resinous polymer being selected from the group consisting of polymers formed by the condensation of formaldehyde and a member selected from the group consisting of phenols, urea and melamines; said elastomeric polymer being in an amount from 10 to 100 parts and said resinous polymer being in an amount from ½ to 5 parts per 100 parts of fiber.

2. A process in accordance with claim 1 wherein the elastomeric polymer is added to the slurry of fibers in the form of an aqueous latex thereof.

3. A process in accordance with claim 2 wherein the elastomeric polymer comprises a copolymer of butadiene and a monomer copolymerizable therewith adapted to and in proportion sufficient to render the copolymer elastic and rubbery.

4. The method of claim 1 wherein at least part of the elastomeric polymer is composed of a copolymer of butadiene and acrylonitrile and the resinous polymer comprises a urea-formaldehyde condensation product.

5. The method of preparing a normally tacky and pressure-sensitive adhesive tape capable of being wound upon itself in roll form and unwound therefrom without substantial delamination thereof which comprises forming an aqueous slurry of cellulosic fibers, incorporating an elastomeric polymer into said slurry, precipitating said elastomeric polymer on said fibers by adding to said slurry a water-soluble polymer having at least three functional groups capable of substantial ionization in water, sheeting the fibers and precipitated elastomeric polymer to form a bonded fibrous web thereof, incorporating into said formed web a resinous polymer incompatible with said elastomeric polymer, said resinous polymer being selected from the group consisting of polymers formed by the condensation of formaldehyde and a member selected from the group consisting of phenols, urea, and melamines, said elastomeric polymer being in amount 10 to 100 parts and said resinous polymer being in amount from ½ to 5 parts per 100 parts of fiber, and then coating at least one major surface of said cellulosic fibrous web with a normally tacky and pressure-sensitive adhesive composition.



6. The method as defined in claim 5 wherein the elastomeric polymer comprises a copolymer of butadiene and a monomer copolymerizable therewith adapted to and in proportion sufficient to render the copolymer elastic and rubbery.

7. The method as defined in claim 5 wherein the elastomeric polymer is composed of butadiene and acrylonitrile and the resinous polymer comprises a urea-formaldehyde condensation product.

8. The method as defined in claim 5 wherein the elastomeric polymer is composed of butadiene and acrylonitrile and the resinous polymer comprises a phenol-formaldehyde condensation product.

9. The method as defined in claim 5 wherein the elastomeric polymer is composed of butadiene and acrylonitrile and the resinous polymer comprises a melamine-formaldehyde condensation product.

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