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FLEXIBLE WEB COATED WITH AN ETHYL
CELLULOSE COMPOSITION

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1 Claim. (Cl. 117—122)

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The object of the present invention is to provide an adhesive which may be applied to paper and other webs, labels, wrappers, and used in various other applications, and which is characterized by non-blocking at normal temperatures, which will be stable for long periods of time and which, when activated by heat, will acquire strong adhesive properties and will retain a tacky and adhesive property for a desired period of time, whereupon inherent crystallization progressively occurs to remove the tacky characteristic.

For many years efforts have been made to produce an adhesive composition which will be dry and stable on a carrying web, which will specifically be non-blocking under normal temperatures, but which can be rapidly activated by heat to become tacky and strongly adhesive with a delayed set, and a specific object of the present invention is to provide an improved adhesive of such type.

Adhesives of the stated type have many useful applications. In the packaging of many products, heat-sealing materials of the general types in use are not applicable because heating irons cannot be applied to the laps and folds of the wrappers without damage to the packaged materials, and my adhesive composition removes the necessity for such method of heat-sealing. A second example of utility is present in the use of labels for high speed bottle-labeling machines, which function at speeds upwards or beyond three hundred applied labels per minute. A minimum of eight seconds of retained tack after the activated label has reached room temperature is required to insure consistently satisfactory operation of such labeling units. Should, however, the machine be stopped for any unforeseen cause, such as bottle breakage, loss of tack after eight seconds would necessitate removal of those labels on those bottles in the rotary labeling unit that had not completed the pressing cycle required to insure intimate contact of the activated coated label to the glass surface. Thus the tack or adhesive character of the label should be retained after the label has reached room temperature and for at least several minutes, so that should the necessity arise for stopping the labeling machine to remove one or more broken bottles or otherwise clean the labeling unit, labels not yet pressed on their bottles may be effectively pressed into firm bonding after such delay.

In order to provide a delayed set adhesive for general use, it should be essentially odor-free and water insoluble. Thus labeled beverage

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bottles are placed in either a refrigerator or immersed in a water tank maintained at low temperatures to effect cooling of the beverage prior to consumption, and should be essentially non-toxic and water insoluble. Were the label coating soluble in water, or were it to contain constituents that tended toward leaching or removal in the presence of high humidity or submersion in a water cooling tank, the labels would float off the beverage bottle, causing loss of identity of the beverage contained therein.

Commercial production of wrappers and labels requires that they be printed or otherwise decorated in large sheets or roll form; subsequent to further processing and cutting into the final smaller sizes. Pressures caused by the roll formation of webs and the stacking of large sheets or labels or the web tension required in web printing processes to insure satisfactory re-wind of the printed labels, and storage conditions under rather high temperatures, are such that complete absence of tack or adhesive character of the coating is required. Under such conditions, my adhesive adequately meets these requirements. Furthermore, a large percentage of wrappers and labels are currently embossed to provide for a more pleasing effect. The applied adhesive should, therefore, provide sufficient flexibility to permit of satisfactory embossing of the coated label stock, and my adhesive composition meets this requirement. Also, the applied label coating should have satisfactory adhesion to glass or other surfaces to which the label is applied, after activation, and should obviously retain this adhesive character for extended periods of time, without material deterioration of its adhesive character even under conditions of high humidity.

Conventional bottle-washing practices employ aqueous sodium hydroxide solution to effect removal of the applied label. Labels of aluminum foil or foil-on-paper labels react with the sodium hydroxide solution to form sodium aluminate. My adhesive coating does not react with the sodium aluminate.

My delayed tack coating consists of a film former such as ethyl cellulose, together with a plasticizer that is unique in that it is normally solid or crystalline at room temperature, but possesses the peculiar characteristic of remaining fluid for an extended period of time prior to crystallizing. The effect of delayed crystallization of solids normally solid at room temperature is extremely limited to at most three or four known substances. The preferred crystalline material exhibiting this unique delayed

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crystallization effect is ortho terphenyl inasmuch as it complies with the greater number of the properties necessitated by the sheet coating, which have been previously indicated.

As an example of a preferred formula:

	Percent
Ortho terphenyl -----	52.50
Ethyl cellulose (46.8-48.5% contained ethoxyl having a viscosity of 4 cps. when 20% by weight of this cellulose ether is dissolved in a solvent solution consisting of 80% toluol and 20% ethanol) -----	17.50
Acetone -----	18.75
Isopropyl alcohol (80%) -----	11.25

Although the lower boiling alkyl alcohols are poor solvents for ortho terphenyl, a mutual solvent for both the ethyl cellulose and the ortho terphenyl can be employed to effect solution of both constituents and the solvent solution will have some tolerance for the alkyl alcohol. In practice, a very low boiling solvent for both the ethyl cellulose and the ortho terphenyl is selected, such as acetone, methyl ethyl ketone, or ethyl acetate, (99% ester) and an alkyl alcohol is selected having a slower evaporating rate than the selected solvent, such as ethyl or isopropyl alcohol. The percentage of selected alcohol is carefully maintained to a point above which precipitation of the ortho terphenyl occurs.

In production practice, the paper, foil or paper mounted aluminum foil is coated with the composition indicated previously, by any standard means, and the coated web is thereupon caused to pass through an oven section, whereupon air maintained at room temperature (not to exceed 120° F.) is thereupon caused to pass over the surface of the coated web, effecting removal of the solvent constituents. In practice, the mutual solvent constituent, such as acetone, evaporates first, leaving a coating containing isopropyl alcohol and precipitation with spontaneous crystallization of the coating occurs.

As a second example:

	Percent
Ortho terphenyl -----	52.50
Ethyl cellulose (46.8-48.5% contained ethoxyl exhibiting a viscosity of 4 cps. when 20% by weight of this cellulose ether is dissolved in a solution consisting of 80% toluol and 20% ethanol) -----	17.50
Hexane -----	22.50
Anhydrous ethanol -----	7.50

The following means have been developed to provide for acceleration of the crystallization of the coating:

(a) The coating is applied to the paper web, dried by passage of heated air over the surface of the coated web, a thin layer of selected lubricant such as oil, wax or soap is applied to the tacky coating by spray application or by coating rolls, and the surface is thereupon subjected to a brushing operation, accelerating the crystallization and permitting immediate re-wind or sheeting of the tack-free web. The employment of a lubricant is required to avoid adhesion of the brush to the tacky coated surface.

(b) The coating is applied to the paper web, dried by passage of heated air over the surface of the coated web, and a thin layer of selected solvent is applied over the surface of the dried web, and the solvent is thereupon caused to be removed by passage of air no higher than room temperature (not to exceed 120° F.). Selection

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of the solvent is of considerable importance. Any solvent in which the ethyl cellulose is soluble but which exhibits poor or no solvent action on the ortho terphenyl has been discovered to be satisfactory. For example, all the lower alkyl alcohols, such as methyl, ethyl, iso-propyl, propyl and others, all of which exhibit poor solvent action on ortho terphenyl, but which have pronounced solvent action on the ethyl cellulose have been discovered to be satisfactory.

(c) The coating is applied to the paper web, dried by passage of heated air over the surface of the coated web, and finely divided or powdered ortho terphenyl in solid crystalline form is caused to be sprayed over the surface of the web. The solid crystalline ortho terphenyl seeds and effects rapid crystallization of the coating.

Both formulae are capable of wide variation to effect a greater or lesser degree of tack or adhesive character. The higher the ortho terphenyl to ethyl cellulose ratio, the more tacky will be the final product, and conversely the lower the ortho terphenyl to ethyl cellulose ratio, the less tacky will be the final product, a minimum of 2.5% ethyl cellulose, balance ortho terphenyl to 100% is believed to be the lowest concentration that would function successfully. A maximum of 82.5% ethyl cellulose, balance ortho terphenyl to 100% is believed to be the highest ethyl cellulose concentration that would function satisfactorily. In practice, although the higher character of ortho terphenyl increases the tack or adhesive character of the coating, film strength and adhesive character of the coating reach an optimum when the coating composition follows the formulae indicated previously.

Substitution of the ethyl cellulose type can be effected without materially affecting the adhesive character and properties of the coating. For example any ethyl cellulose containing 43.5 to 50% contained ethoxyl and varying from 2 cps. to 500 cps. (exhibiting this viscosity when a 20% solution of the cellulose ether is dissolved in a solvent combination consisting of 80% toluol, 20% ethanol). In addition, it is entirely possible to substitute other film formers such as nitrocellulose, benzyl or other aryl cellulose, methyl or other alkyl cellulose, mixed cellulose esters, such as cellulose aceto-butyrate or aceto-propionate, vinyl halides, vinyl acetate, mixed vinyl co-polymers, such as vinyl chlor-acetate, acrylic and methacrylic acid ester polymers, polymers and co-polymers of styrene, polymers and co-polymers of vinylidene halide, abietic acid esters and most other resinous compatible products for the ethyl cellulose.

Although the ortho isomer of terphenyl is remarkable and completely unique in its exhibition of delayed crystallization at normal room temperatures (35° to 120° F.) other substances also exhibit this delayed crystallization tendency to a lesser degree and in consequence can also be employed to produce delayed tack adhesive coatings. These include diphenyl and the other two isomers of terphenyl, the meta and para.

The ortho terphenyl-ethyl cellulose preferred composition has functioned successfully on labels subject to washing in existing rotary label and bottle washing equipment employing sodium hydroxide solutions exhibiting no untoward effects in the wash tanks. Accelerated removal of said labels can be secured by the incorporation of aluminum, zinc or magnesium powder to the coating composition and to the extent of from 1 to 25% (perferred 7.5% aluminum powder)

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which in turn tends towards a more pronounced and more rapid reaction with the sodium hydroxide solution.

It will be understood that in any or all of the compositions given herein, an additional plasticizer may be added whenever it is desired to secure increased plasticity.

A further example which employs a film former other than that specified in the first two examples, is as follows:

Example 3

	Percent
Ortho terphenyl	28.22
1/2 second nitrocellulose containing 10.7 to 11.2% nitrogen	8.71
Methyl ethyl ketone	14.27
Isopropyl alcohol (85%)	48.80

In the following example, the film former selected is polyvinyl acetate:

Example 4

	Percent
Ortho terphenyl	32.87
Polyvinyl acetate (having a viscosity of 15 cps. when 5% by weight of this resin is dissolved in methanol)	9.83
Methyl ethyl ketone	2.10
Acetone	8.22
Ethyl alcohol (8.7%)	41.98

In the following example, the film former proportion substantially exceeds that of the ortho terphenyl or equivalent material having delayed crystallization effect:

Example 5

	Percent
Ortho terphenyl	11.50
Ethyl cellulose (46.8-48.5% containing ethoxyl) having a viscosity of 4 cps. when 20% by weight is dissolved in a solvent solution consisting of 80% toluol and 20% ethanol	36.34
Acetone	9.22
Isopropyl alcohol (80%)	42.94

As a further example:

Example 6

	Percent
Meta terphenyl	26.72
Ortho terphenyl	24.12
Ethyl cellulose (46.8-48.5% containing ethoxyl) having a viscosity of 4 cps. when 20% by weight is dissolved in a solvent solution consisting of 80% toluol and 20% ethanol	15.12
Acetone	18.37
Isopropyl alcohol	15.67
Apply to web at solution temperature of 125°-130° F.	

As an additional example:

Example 7

	Per cent
Ortho terphenyl	33.75
Para terphenyl	22.12
Methyl phthalyl ethyl glycolate	4.73
Ethyl cellulose (46.8-48.5% containing ethoxyl) having a viscosity of 7 cps. when 20% by weight of this cellulose ether is dissolved in a solvent solution consisting of 80% toluol and 20% ethanol	13.67
Hexane	4.28
Toluol	2.25
Anhydrous ethanol	9.20

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Apply solution at temperatures from 125°-130° F. because of the low solubility of the para terphenyl in the composition at room temperature.

As a further example:

Example 8

	Per cent
Diphenyl	42.87
Ethyl cellulose (46.8-48.5% containing ethoxyl) having a viscosity of 7 cps. when 20% by weight of this cellulose ether is dissolved in a solvent solution consisting of 80% toluol and 20% ethanol	14.23
Heptane	21.11
Toluol	2.25
Anhydrous ethanol	6.33

Formulae containing diphenyl may prove advantageous in inhibiting mold growth in products subject to mold growth packaged in wraps prepared with the above coating.

As an additional example:

Example 9

	Per cent
Para terphenyl	38.75
Ethyl cellulose (46.8-48.5% containing ethoxyl) having a viscosity of 4 c. p. s. when 20% by weight of this cellulose ether is dissolved in a solvent solution consisting of 80% toluol and 20% ethanol	15.23
Hexane	24.25
Toluol	3.12
Anhydrous ethanol	18.65

This coating solution should be applied at temperatures from 125°-130° F. because of the low solubility of the para terphenyl in the solvent composition at room temperature and is not a preferred composition.

It will thus be seen that by means of the invention there is provided a homogeneous normally-solid coating for flexible webs and other carriers, which comprises a film-forming material, and a material normally solid at room temperatures, the composition being capable of activation by heat to assume a tacky adhesive form for an extended period of time and to progressively crystallize to a non-tacky solid.

Further utility of the invention lies in the following characteristic of the coating:

Through the progressive crystallization of the coating after it has assumed adhesive character through the application of heat, adhesive layers of intermediate labels, for example, and containers to which the labels are affixed, become "dry." At the same time the said "dry" adhesive does not lose its ability to become fluid and tacky when again heated. Thus in the case of labels on bottles, such labels may be removed by stripping after the application of heat. There are many further applications where this characteristic of the adhesive coating finds special utility.

Accelerated crystallization of the initially applied coating, after evaporation of the solvent, by brushing action, as herein specified, may be substituted by any suitable surface agitation of the coating, vibration for example, or by induced crystallization through any other suitable means, as by pressure contact with hard small aggregates bonded to a flexible carrier or by the solvent film method described herein.

Having described my invention, what I claim

and desire to secure by Letters Patent, is as follows:

A flexible web having on a surface thereof a normally dry coating composition having delayed adhesive properties when subjected to heat above room temperature which comprises a minor proportion of ethyl cellulose, and ortho terphenyl in major proportion.

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