

UNITED STATES PATENT OFFICE

2,570,561

ADHESIVE COMPOSITION

Walter B. Kinney, Bainbridge, N. Y., assignor to
The Borden Company, New York, N. Y., a cor-
poration of New Jersey

No Drawing. Application July 8, 1946,
Serial No. 682,139

12 Claims. (Cl. 106—146)

1

This invention relates in general to adhesive compositions, and in particular to adhesives for fastening labels to bottles which are subject to immersion in ice and water.

Beverages such as soft drinks, beer, and the like are often chilled by placing them in a metal container filled with ice or ice water prior to serving. Most of such bottled beverages are supplied with a label which identifies the contents and which advertises the product of the manufacturer. When ordinary adhesives are used for gluing the labels to the bottles, such as adhesives made from mixtures of animal glue and starch, it often happens that such labels become detached from the bottles upon contact with the ice or the water, and as a result the labels peel off and become lost. Thus, when there are several varieties of beverages in the container there is usually no means for identifying the contents, and mistakes arise in filling orders. Moreover, there is the loss of the advertising value of the printed material on the label when the label is loosened or becomes detached from the bottle.

Attempts have been made to provide an improved adhesive which does not readily separate from the label or bottle and which is resistant to water and ice. In U. S. 2,351,109, granted to Corwin and White on June 13, 1944, and the continuation-in-part, U. S. 2,351,309 to White issued on the same day, there is described and claimed an improved adhesive for use in labeling bottles which are subject to such conditions as aforementioned. The adhesives described in the aforementioned patents are resistant to ice or ice water as well as those temperatures of the water which may result when the ice becomes melted and warms up to room temperature, as occurs when the containers in which the bottles are placed are not replenished with ice as frequently as they should be, or where the bottles are permitted to stand in such containers overnight or over the week end. There is thus provided an adhesive which does not readily loosen or peel up to several days at temperatures ranging from about 32° F. to 70° or 80° F. when subjected to immersion.

The present invention is directed to an improvement upon the inventions described in the aforementioned patents. The adhesive composition of the present invention is so modified as to extend its uses to include other conditions to which such labeled bottles may be subjected and which are not met by the aforesaid prior compositions.

A great deal of difficulty has been encountered

2

where labeled bottles of the class described are immersed in a metal container which contains water and/or ice having an alkaline pH, for example a pH of about 8 or thereabove. It is often the practice in soda fountains or other establishments dispensing bottled beverages to add more ice as the ice melts, without washing or cleansing the container. As a result of such practice, an odor develops in a comparatively short time, particularly in warm weather, due to the melting ice and other casual contamination, even when the operator drains away part of the water to make way for more ice but fails to cleanse the container or remove the contaminating substances. The contamination and odor persists even after fresh ice is added. The operator, as a substitute for his formula to clean out the container, usually adds an alkali such as borax or soda ash to neutralize the odor. There is no fixed percentage of alkali added; the operator simply throws in a handful or two, and this appears to eliminate the disagreeable odor. It has been found as a result of the addition of such alkali, labels adhered to glass bottles with the prior adhesives aforementioned quickly peel and become loosened, especially when the water becomes warmed to room temperatures.

It was, therefore, a general object of the present invention to overcome disadvantages encountered in the use of prior adhesives.

It was a further object of the invention to improve upon and extend the advantages of the adhesives described in the patents to Corwin and White.

It was a specific object of the invention to provide an improved adhesive for use in paper gluing, particularly for use as a label paste.

It was still another object of the invention to provide an adhesive which will withstand soaking in both ice water and water at room temperature or thereabove, especially wherein the pH of the water is alkaline.

Another object of the invention was to provide an adhesive which could be satisfactorily used in high speed labeling machines, which was non-stringing and which had a good stability, working life and a fast-setting action.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

In accordance with the present invention there is now provided an adhesive composition which is particularly suitable for use as a label paste and which is highly resistant to alkaline liquids, which composition comprises casein, an alkaline solvent for said casein, a chromium compound

and an aqueous dispersion medium. In a now preferred embodiment of the invention there may be added to the adhesive various modifying substances such as thickeners, preservatives, foam abaters, and flow promoters which are hereinafter set forth and described in detail.

The invention accordingly comprises a composition of matter possessing the characteristics, properties, and the relation of components, and articles produced therefrom which will be exemplified in the composition hereinafter described, and the scope of the invention will be indicated in the claims.

The adhesive composition of the present invention was developed as the result of lengthy research. The adhesive composition provides a tenacious bond between the label and the bottle even after it is immersed in a highly alkaline solution for a long period of time. Under actual tests, it has been found that labels glued to glass bottles and the like employing the present adhesive remain intact and in good condition for several days when immersed in a strongly alkaline solution, for example a solution having a pH of 10.0, even when the temperature of the water is raised as high as 90° F.

Casein is preferably employed as the tacky base material used in compounding the adhesive. In the now preferred embodiment there is employed an acid-precipitated casein which has been air dried and ground to about 20 to 30 mesh.

For the alkaline solvent used in forming the adhesive there may be employed an alkaline material such, for example, as potassium hydroxide, sodium hydroxide, ammonium hydroxide, sodium carbonate, potassium carbonate, soda ash, borax, potassium phosphate, sodium phosphate, and the like. In the preferred embodiment there is employed ammonium hydroxide of about 26° Bé. as the alkaline solvent.

Water is the aqueous solvent preferably employed for forming the liquid adhesive, but other aqueous media may be employed to dissolve the various ingredients, such, for example, as mixtures or solutions of organic solvents and water. Various amounts of the aqueous solvent may be employed, depending upon the thickness desired for the final product. The amount of the aqueous solvent employed in the preferred embodiment comprises from 275 to 600 parts by weight.

For the chromium compound employed in forming the adhesive there may be used as a class any of the well-known chromium compounds, such, for example, as metallic salts of the chromates such as those formed of barium, calcium, lithium, magnesium, aluminum, copper, lead, and the like. There may also be employed chromium salts of organic and inorganic acids such as the oxalates, nitrates, sulfates, carbonates, bromides, borates, chlorides, acetates, fluorides, and the like. There may be used in forming the adhesive composition about 7 to 35 parts by weight of such chromium compounds for each 100 parts of casein employed.

There may also be employed in forming the adhesive various modifiers and assistants, such, for example, as thickeners, preservatives, flow promoters, and the like, as desired.

In a now preferred embodiment of the invention, there may be combined with the adhesive composition a flow promoter comprising an organic amide such, for example, as urea, thiourea, formamide, acetamide, ammonium thiocyanate, and the like. There may be used a fairly large

amount of the flow promoter, even exceeding slightly the amount of casein employed.

In order to prevent excess foaming of the adhesive when used in a labeling machine or other mechanical device, there may be employed in forming the adhesive composition various foam abating agents such, for example, as tributyl citrate, tributyl phosphate, amyl citrate, pine oil, octyl alcohol, capryl alcohol, and the like. The amount of foam abater which may be employed can be varied over a wide range, but usually less than 4% is required based on the amount of casein employed.

Various preservatives may be used in forming the adhesive to prevent the casein from decomposing and putrifying, such, for example, as ethyl para-hydroxybenzoate, para-chloro-metacresol, sodium ortho-phenyl phenate, sodium meta-chlorophenol, carvacrol, and the like. The amount of preservative used in the adhesive may be varied between wide limits, but it is not usually necessary to employ over 5% by weight of the weight of the casein used.

Various thickeners may be added to the adhesive composition if it is desired to form a heavier or more viscous product, as, for example, hydrophilic cellulose ethers, polyvinyl alcohol, linseed meal, pectins, pectates, bentonite, and the like. A thickener which has been found particularly useful for this purpose comprises bentonite, but it is to be understood that such other thickeners may be employed which produce the physical function of maintaining the proper consistency of the adhesive over a range of temperatures such as between 60° F. and 100° F. It may be desirable to add to the adhesive up to 15% of such thickener, based upon the amount of casein used in the formula.

The following examples are given by way of illustration but not by way of limiting the invention. All parts, unless otherwise indicated, are by weight.

Example 1

	Parts
Acid precipitated casein 30-mesh.....	100
Water	600
Ammonium hydroxide 26° Bé.....	7
Magnesium chromate	10.5

The following has been found to be a convenient method for preparing the adhesive:

The 600 parts of water were placed in a steam jacketed kettle. To this there was then added 100 parts of acid precipitated casein, preferably ground to about 30-mesh. The agitator in the kettle was then started and the mixing continued until the casein was thoroughly wet. To the contents of the kettle there was then added the 10.5 parts of magnesium chromate while the mixing was continued, after which there was then added the 7 parts of 26° Bé. ammonium hydroxide. Steam was next turned into the jacket surrounding the kettle and the mass heated while mixing until the temperature of the mixture was about 140° F. to 160° F. This temperature was maintained, and the mixing continued until the casein was thoroughly dissolved.

The mass was then permitted to cool. The adhesive thus formed was found to be a rather heavy flowing material at ordinary room temperatures, but ran well in a labeling machine at elevated temperatures. The adhesive when used as a coating for paper or when used as an adhesive for labeling bottles was found to have superior properties over prior adhesives heretofore employed. The adhesive did not readily peel from

5

the glass bottles when immersed in a strongly alkaline solution for several days having a pH of about 10, at all temperatures ranging from 32° F. to 90° F. Best results are attained if the adhesive is permitted to dry and age for a short period of time after application to the bottles and prior to commercial use.

Example 2

	Parts
Casein -----	100
Water -----	600
Borax -----	12
Powdered aluminum chromate -----	10.5

The adhesive was prepared in the same manner recited in Example 1. The ingredients were added to a steam jacketed mixing vessel and dissolved as outlined therein. This adhesive composition was found to be very satisfactory when subjected to alkaline water at temperatures up to 90° F. for three days.

Example 3

	Parts
Casein -----	100
Water -----	600
Ammonium hydroxide 26° Bé -----	7
Chromium acetate -----	10.5

The same procedure for dissolving and preparing the adhesive was followed as outlined under Example 1. The adhesive had good stability, spreading qualities, and a consistency which permitted its use on high speed labeling machines. It was found that this adhesive was water resistant at temperatures above 80° F. and up to 90° F., as well as being resistant to aqueous liquids having a high alkaline pH.

Example 4

	Parts
Casein -----	110
Water -----	326
Ammonium hydroxide 26° Bé -----	5
Magnesium chromate -----	25

The adhesive was prepared by placing the 326 parts of water in a steam jacketed kettle equipped with an agitator. There was then added the 110 parts of casein, preferably having a fineness of about 30-mesh. The agitator was started and the casein thoroughly wet. The 25 parts of magnesium chromate were then added and stirring continued. The magnesium chromate was preferably powdered to enable it to dissolve more readily. The ammonium hydroxide was then added and the heat turned into the steam jacket of the kettle.

To the mass in the kettle there was then added a flow promoter comprising 98 parts of urea or an equivalent amount of an organic amide. The flow promoter comprising such organic amide had the added function of serving as a dissolving agent for the ingredients, thus assisting in effecting quick solution of the casein.

To the preparation in the kettle there was then added various other agents as thickeners, preservatives, and foam abaters in the following amounts:

	Parts
Bentonite -----	8
Ethyl para-hydroxybenzoate -----	1
Tributyl citrate -----	1

There was first added the bentonite thickener, and after it had been thoroughly dispersed throughout the mixture, there was then added the ethyl para-hydroxybenzoate preservative. Fin-

6

ally there was introduced the foam abater comprising the tributyl citrate. During the mixing, the temperature of the mass was gradually raised to approximately 180° F. by means of the steam jacket surrounding the kettle, and held at that temperature until a smooth, homogeneous adhesive resulted. Thereupon the heat was turned off and the mixture allowed to cool to room temperature. On testing it was found that the adhesive had a good working life, did not string when used in high speed labeling machines, and was resistant to soaking in alkaline media up to temperatures of 90° F. for several days.

Example 5

	Parts
Casein -----	110
Water -----	326
Ammonium hydroxide 26° Bé -----	5
Lithium chromate -----	25

The procedure outlined under Example 4 was followed. To the uniform dispersion there was then added 124 parts of thiourea and mixing continued until it was substantially dissolved. To this mixture there was then added a thickener, a preservative, and a foam abater in the following amounts:

	Parts
Bentonite -----	8
Ethyl para-hydroxybenzoate -----	1
Tributyl citrate -----	1

After stirring until there was formed a smooth, homologous mass, during which the temperature was gradually raised to about 180° F., the mass was allowed to cool to room temperature. When tested under conditions set forth above, it was found that the adhesive had good stability and was resistant to alkaline water having a pH of about 10.0, remaining firmly attached to a glass bottle for several days at temperatures up to 90° F.

Example 6

	Parts
Casein -----	110
Bentonite -----	8
Ethyl para-hydroxybenzoate -----	1
Tributyl citrate -----	1
Water -----	326
Urea -----	98
Ammonia -----	5
Calcium chromate -----	25

The procedure of preparation was the same as in Example 4.

Example 7

	Parts
Casein -----	110
Bentonite -----	8
Ethyl para-hydroxybenzoate -----	1
Tributyl citrate -----	1
Water -----	326
Urea -----	98
Ammonia -----	5
Aluminum chromate -----	25

The procedure of preparation was the same as in Example 4.

Example 8

	Parts
Casein -----	110
Bentonite -----	8
Ethyl para-hydroxybenzoate -----	1
Tributyl citrate -----	1
Water -----	326
Urea -----	98
Ammonia -----	5
Copper chromate -----	25

The procedure of preparation was the same as in Example 4.

Example 9

	Parts
Casein	110
Bentonite	8
Ethyl para-hydroxybenzoate	1
Tributyl citrate	1
Water	326
Urea	98
Ammonia	5
Barium chromate	25

The procedure of preparation was the same as in Example 4.

Obviously, the proportions and ingredients employed may be varied over a wide range of proportions, but the amounts set forth in the foregoing examples have been found to produce very satisfactory results.

In the now preferred embodiment it has been found that the pH of the finished adhesive composition should be approximately 7 to 8, but adhesives having other pH ranges varying somewhat from these values have been found to be satisfactory. In some instances where the finished products are definitely acid as a result of adding a chromium compound which is acid in character, this acidity may be offset by increasing the amount of ammonia added to the mixture so as to produce a pH of approximately 7 to 8.

The adhesive composition possesses exceptionally good keeping qualities and therefore can be shipped and kept in storage for considerable time, for example up to six or eight months, without fermentation and without appreciable change in consistency or viscosity or its water-resistant quality.

The present adhesive has the added advantage over those described in the Corwin et al. and White patents in that it does not readily peel or become dissolved and separate from the label, or does not permit the label to become separated from the bottle when stored in water having a high alkalinity. Moreover, the present adhesive composition will withstand high temperatures, i. e. up to 90° F. and above, before separating from the bottle. Freezing apparently does not harm the product.

The present adhesive composition, like those described in the Corwin et al. and White patents, may also be prepared in dry form and sold as casein glue base, whereupon the water or other aqueous material may be added to the glue base just prior to use. Such glue base comprises a dry mixture of casein, lime, and chromium salt, to which is added if desired a thickener, a foam abater, and a preservative in the proportions set forth.

Heretofore, many of the usual casein glues have contained an added alkaline earth base (lime or hydrated lime, magnesium oxide or hydroxide or equivalent). It will be observed that none of the above formulas include such added alkaline earth bases and, in the appended claims, the expression "free from added alkaline earth bases" is intended to mean freedom from added oxides and hydroxides of calcium, barium, strontium, and magnesium. I am, of course, aware that, according to some of the writers, magnesium is not included in the alkaline earth metals although many of its compounds are much like the corresponding calcium compounds. Freedom from these alkaline earth bases is characteristic of all glues prepared in accordance with the present inven-

tion, and having the properties set forth in this specification.

No claim is made herein to any glue that contains added basic alkaline earth compounds.

Since certain changes may be made in the above composition of matter and different embodiments of the invention could be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

1. An adhesive composition which is highly resistant to alkali solutions at elevated temperatures and to ice water, which composition consists essentially of water as its largest component, casein, an alkaline solvent for said casein in an amount which will dissolve the casein, a soluble chromium compound in an amount less than the casein and a flow promoter comprising an organic amide, said adhesive being free from added alkaline earth bases.

2. An adhesive composition which is highly resistant to alkali solutions at elevated temperatures and to ice water, which composition consists essentially of casein, an alkaline solvent for said casein, a soluble chromium compound, an organic preservative for said casein a flow promoter comprising an organic amide, a foam abater, and an aqueous dispersion medium for said components, said adhesive being free from added alkaline earth bases.

3. An adhesive composition which is highly resistant to alkali solutions at elevated temperatures and to ice water, which composition consists essentially of casein, an alkaline solvent for said casein, a flow promoter comprising an organic amide, a soluble chromium compound, a thickener, and an aqueous dispersion medium for said components, said adhesive being free from added alkaline earth bases.

4. An adhesive composition which is highly resistant to alkali solutions at elevated temperatures and to ice water, which composition consists essentially of casein, an alkaline solvent for said casein, a soluble chromium compound, a flow promoter comprising an organic amide, and an aqueous dispersion medium for said components, said adhesive being free from added alkaline earth bases.

5. An adhesive composition which is highly resistant to alkali solutions at elevated temperatures and to ice water, which composition consists essentially of casein, an alkaline solvent for said casein, a soluble chromium compound, urea, and an aqueous dispersion medium for said components, said adhesive being free from added alkaline earth bases.

6. An adhesive composition which is highly resistant to alkaline solutions at elevated temperatures and to ice water, which composition consists essentially of components in approximately the following proportions:

	Unit parts by weight
Water	326
Casein	110
Ammonium hydroxide 26° Bé	5
Bentonite	8

Unit parts by weight	
Ethyl para-hydroxybenzoate-----	1
Tributyl citrate-----	1
Soluble chromium compound-----	25
Urea-----	98

said adhesive being free from added alkaline earth bases.

7. An adhesive composition which is highly resistant to alkaline solutions over a temperature range between 32° F. and 100° F. consisting essentially of 100 parts by weight of casein, from 275 to 600 parts by weight of water, approximately 7 parts by weight of 26° Bé. ammonium hydroxide, and approximately 10.5 parts by weight of magnesium chromate; the water and ammonium hydroxide serving as solvent for the casein; the magnesium chromate serving to develop water, temperature, and alkali resistance; the composition being free from alkaline earth metals.

8. An adhesive composition which is highly resistant to alkaline solutions at temperatures within the range between 32° F. and 100° F. consisting essentially of 100 parts by weight of casein, 275 to 600 parts by weight of water, approximately 12 parts by weight of borax, and approximately 10.5 parts by weight of powdered aluminum chromate, the composition being free from alkaline earth metals.

9. An adhesive composition which is highly resistant to alkaline solutions at temperatures within the range between 32° F. and 100° F. consisting essentially of 100 parts by weight of casein, from 275 to 600 parts by weight of water, approximately 5 parts by weight of 26° Bé. ammonium hydroxide, approximately 25 parts by weight of magnesium chromate, approximately 8 parts by weight of bentonite, approximately 1 part by weight of ethyl para-hydroxybenzoate, and approximately 1 part by weight of tributyl citrate, the composition being free from alkaline earth metals.

10. An adhesive composition which is highly resistant to alkaline solutions at temperatures within the range between 32° F. and 100° F. consisting essentially of 100 parts by weight of casein, from 275 to 600 parts by weight of water, approximately 5 parts by weight of 26° Bé. ammonium hydroxide, approximately 25 parts by weight of lithium chromate, approximately 8 parts by weight of bentonite, approximately 1

part by weight of ethyl para-hydroxybenzoate, and approximately 1 part by weight of tributyl citrate, the composition being free from alkaline earth metals.

11. An adhesive composition which is highly resistant to alkaline solutions at temperatures within the range between 32° F. and 100° F. consisting essentially of 110 parts by weight of casein, approximately 326 parts by weight of water, approximately 8 parts by weight of bentonite, approximately 1 part by weight of ethyl para-hydroxybenzoate, approximately 1 part by weight of tributyl citrate, approximately 98 parts by weight of urea, approximately 5 parts by weight of 26° Bé. ammonium hydroxide, and approximately 25 parts by weight of calcium chromate, the composition being free from other alkaline earth metals than the calcium chromate.

12. An adhesive composition which is highly resistant to alkaline solutions at temperatures within the range between 32° F. and 100° F. consisting essentially of casein in the proportion of 110 parts by weight, water in the proportion of approximately 326 parts by weight, bentonite in the proportion of approximately 8 parts by weight, ethyl para-hydroxybenzoate and tributyl citrate in the proportion of approximately 1 part by weight of each, urea in the proportion of approximately 98 parts by weight, 26° Bé. ammonium hydroxide in the proportion of approximately 5 parts by weight, and copper chromate in the proportion of approximately 25 parts by weight, the composition being free from alkaline earth metals.

WALTER B. KINNEY.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,986,991	Clickner	Aug. 7, 1934
2,351,109	Corwin et al.	June 13, 1944
2,401,919	Ender	June 11, 1946

FOREIGN PATENTS

Number	Country	Date
405,381	Great Britain	Feb. 8, 1934
543,302	Great Britain	Feb. 18, 1942