Patented Aug. 14, 1945 2,382,417

UNITED STATES PATENT OFFICE

2,382,417

DISPERSIONS OF ADHESIVES OF THE OIL-IN-WATER TYPE

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No Drawing. Application February 28, 1940, Serial No. 321,289

25 Claims. (Cl. 260—741)

The present invention relates to adhesive compositions or dispersions of the oil-in-water type. It especially concerns water dispersions comprising polyvalent metal soaps or polyvalent metal resinates, which occur largely or entirely in the dispersed phase.

My invention also, in one intended embodiment thereof, contemplates compositions containing rubber. The rubber, where used, may be present in relatively small proportion or in relatively large proportion in relation to other ingredients of the composition, depending upon the particular use which the resulting composition is intended to serve.

While the compositions of the present invention have a wide variety of uses, important uses of the same are illustrated by bottle label cements, tabbing cements, dry-seal adhesives for envelopes, packages and the like, trim cements adapted for use in the automotive trade where trim cloth may be adhesively joined to composition board, and the like.

Not by way of limitation, but rather to illustrate an important aspect of the present invention, particular consideration will first be given to the problem of bottle label cements. Rubber cements of the so-called solvent type, e. g. where a rubber solvent such as gasoline, petroleum spirits or other hydrocarbon solvent is employed, have the disadvantage that they will not wet a surface which is already wet with water. Since it is commonly necessary or desirable to apply labels to bottles immediately after they have come from the washer, pasteurizer, etc., (depending upon the particular product to be bottled), it is highly desirable, if not essential from a practical point of view, to employ an adhesive which will wet a surface which is wet with water. Thus gasoline or other hydrocarbon solvent types of cements are disadvantageous. Various adhesives in the form of water "solutions" are available and have been employed as bottle label adhesives, for example glue "solutions." These materials have the capacity of wetting surfaces already wet by water but they deposit, upon evaporation, an adhesive film that may be re-dissolved in water. This, as will be obvious, has the disadvantage of allowing labels, joined to containers or bottles with glue or the like, to become loosened and fall off, for example upon extended immersion in water or cooling baths.

It is desired to supply a label adhesive which will wet a surface which is already wet with water and which will be waterproof in the form of the final dry film. It is also a purpose of this invention to supply such a label adhesive which is relatively colorless or of a pale color, so as not to disfigure or harm the appearance of glass bottles, metal cans or the like on which labels are to be applied.

I have found that by employing water dispersions of water-insoluble materials, as distinguished from water "solutions" of water-soluble or hydrophyllic colloids, I am able to provide compositions which, upon application, will wet surfaces already wet with water and then, after drying, will provide a substantially waterproof film. I have also found, by employing a particular class of compositions hereinafter illustrated, that I can secure a bottle label or can label adhesive of desired color, adhesive strength, cheapness and other desired properties. I have also found that, by suitable control of ingredients as hereinafter illustrated, my bottle label adhesive is of such a type that labels applied therewith can be readily removed, for example during the course of cleaning and washing the bottles for refilling, with an aqueous solution, e. g. a 5% sodium hydroxide solution which is heated.

The element of cost is an important, if not a controlling element, within limits, in adhesives of this type. Glue "solutions" and the like, heretofore used as bottle label adhesives, are quite cheap and, despite the disadvantages which these materials possess of allowing labels to loosen and fall off before the goods reaches the customer, as where the same is packed in ice or ice-water, from a practical point of view these materials cannot be replaced by any adhesive unless it at least approaches in price that of the glue or modified glue "solutions" heretofore used.

However, as above indicated, the principles which apply to the bottle label adhesives of the present invention, likewise apply to a large extent to adhesives useful for a variety of other purposes.

An important object of this invention is to produce an oil-in-water type dispersion containing a

substantial proportion of a polyvalent metal soap. A further object is to provide an oil-in-water type dispersion in which a polyvalent metal soap or polyvalent metal resinate, e. g. zinc and/or calcium abietate, makes up a substantial proportion of the dispersed phase of the dispersion, that is makes up 5%, 10% or more, up to about 50 or 75%, or possibly more, of the dispersed phase; and in which a restricted amount of alkali metal soap may be present in the continuous phase, the amount of the alkali metal soap being for example present to the extent of less than 10% and preferably less than 7.5% of the dispersed phase. In certain cases, the alkali metal soap may be present in amounts between 0 and 5%, or may be entirely absent. While it is an important object of my invention to produce improved dispersions having a pH greater than 7, the present invention comprehends dispersions or adhesives having a lower pH, e. g. of the general order of 7.

A further object of this invention is to provide dispersions comprising a mixture of rubber, (e. g. rubber applied in the dry form or as latex and/or reclaimed rubber and/or synthetic rubber-like materials) and a polyvalent metal soap or resinate, said mixture being dispersed in an aqueous vehicle, and to render such dispersions stable. It is also an object of this invention to produce such rubber-polyvalent metal resinate dispersions which are of small particle size.

A further and salient object of the present invention is to employ materials, of which proteins are an example, as an element of my compositions which makes possible the production of an aqueous dispersion containing large amounts, or a high proportion, of polyvalent metal resinates in the dispersed phase.

In one aspect of my invention a contemplated and preferred procedure involves the introduction of rubber in the form of latex into a plastic mixture, e. g. involving polyvalent metal resinates, etc., so as thereby to secure the admixture of rubber in undegraded state with the resinous material in any desired amount, even though the amount be relatively minor in relation to the remaining solids of the dispersed phase.

The above and other objects and advantages will appear from the description taken as a whole.

It will be observed that if an attempt were made to produce a dispersion of, for example, zinc rosinate, calcium rosinate, or the like with or without rubber, in an aqueous vehicle, the tendency would be to produce a dispersion of water in such composition instead of the converse; that is, the tendency would be to produce a water-in-oil type of dispersion. While it is true that by employing large amounts of alkali metal soap, such as sodium or potassium oleate, in relation to the polyvalent metal resinate or the like, an oil-in-water type dispersion can be produced, yet such high proportions of alkali metal soap would render the resulting composition useless for such purposes as those primarily contemplated by the present invention. Due to the high amount of water soluble soap, the final dried film of such a composition would not be water-resistant and would be unsatisfactory in various other respects. However, in accordance with the present invention, by employing certain materials such as proteins, protein derivatives, high molecular weight polysaccharides and derivatives thereof, I have prepared dispersions of polyvalent metal resinates (and rubber) in water with the use of only a minor proportion of alkali metal soaps, and even have produced such compositions in the absence of alkali metal soaps.

To better illustrate my invention a number of specific formulae will be given.

Formula 1

Mineral oil	grams	625
Pale Zitro	do	750
WG rosin	do	125
Latex (60% solids)	do	150
Casein	do	42
Methyl cellulose	do	21
50% KOH soln	do	46
Water	do	1320
Isopropanol	cc	177
N-butanol	cc	30
Ethyl acetate	cc	59

The "Zitro" of the above composition is a pale or light amber colored zinc treated rosin having a low acid number as compared with ordinary rosin. The acid number is about 15 and the metallic zinc content of the Zitro is approximately 4.8%, the zinc of course being present as a zinc rosinate or zinc abietate. Zitro also contains a minor amount of calcium, as calcium rosinate, the metallic calcium being present in sufficient amounts in relation to the zinc so as to preserve solubility of the zinc treated rosin composition in solvents such as gasoline or the above-mentioned mineral oil.

A suitable method for compounding the dispersion cement of Formula 1 is as follows: Place the 750 grams of Zitro in an internal mixer (for example of the Werner-Pfleiderer type) and subject the same to mechanical working with a steam pressure in the jacket of 40 to 100 pounds per square inch gauge and until a smooth plastic mass is obtained. The WG rosin is then added, for example in two or three increments, while continuing the mixing. When the batch is smooth and uniform, the mineral oil is added sufficiently gradually so that the batch retains at all times sufficient mechanical strength or stiffness to work the oil uniformly throughout the same and to avoid the formation of lumps. Preferably the oil is added sufficiently slowly so that it is dissolved in the softened or molten resin as added.

The WG rosin, which serves as the soap-forming acid, is a pale gum rosin having an acid number of about 165 to 170, but other gum or wood rosins may be employed.

Next, while maintaining the temperature of the batch below the boiling point of the water, the liquid latex is added. The latex may be added all at once; however it is usually preferred to add it gradually or in a number of increments. The mechanical mixing is continued until a smooth batch is obtained, with water dispersed in a mixture of rubber, resin, resinates and oil. Next about 150 grams of water and/or ice are added and the mechanical mixing continued until a smooth batch is obtained. Then 42 grams of the 50 per cent KOH solution is added, and may be added all at once. Next the 42 grams of casein dissolved in 126 grams of water and 4 grams of the 50 per cent KOH solution, is added to the batch, while continuing the mixing. Inversion of phase takes place upon the addition of the casein solution, water then becoming the continuous phase and the composition comprising rubber, resin, resinates and oil being dispersed therein. The temperature of the batch is so controlled (by controlling proportions of water and ice and by regulating heat-

exchange fluid or water circulated through the jacket of the internal mixer) that, at the point at which inversion takes place, the batch is within the range of 125° to 165° F., and ordinarily is preferably within the range of 135 to 145° F., or is controlled at a temperature approximating the last mentioned range. In general, within limits, the higher the temperature at which the batch is maintained, the smaller will be the amount of water desired or needed to accomplish inversion of phase; conversely, at lower temperatures, larger amounts of water may be employed, or may be needed, in the batch prior to inversion. However I have found the above range of temperatures advantageous in producing a stable dispersion, of desired small particle size, where a composition such as illustrated in Formula 1 is employed.

Next the methyl cellulose is introduced into the batch in the form of a solution of the 21 grams of methyl cellulose in approximately 400 grams of water. Of course the methyl cellulose may be added in a more concentrated solution and a suitable quantity of water separately added, for example, in increments alternately with increments of the methyl cellulose solution.

Next add all of the remainder of the water, except for approximately 200 grams, and continue the mechanical mixing until the batch is smooth. Then add the isopropanol, n-butanol and ethyl acetate, conveniently as a mixture, and preferably gradually. When these ingredients have been mixed in so that the batch is smooth, further quantities of water may be added to bring the resulting dispersion to the desired viscosity. The isopropanol and/or n-butanol are, of course, water-soluble mono-hydric alcohols and, among the other advantages stated, have the advantage of serving as foam depressants during mixing which used in sufficient proportion, as generally illustrated herein, e. g., the alcohol in combined alcohols making up 10 percent or more of the aqueous phase of the dispersion. Obviously more or less water can be added than shown in Formula 1, depending upon the particular viscosity desired.

In Formula 1 the methyl cellulose and casein both contribute to keeping the polyvalent methyl resinate, i. e. the zinc and calcium abietate of the Zitro, dispersed in the aqueous vehicle. In the absence of the casein and methyl cellulose, the potassium resinate (formed by reaction of the KOH solution with the rosin) would be entirely unable to produce an inversion of phase or to disperse the polyvalent metal resinate and rubber composition in the aqueous vehicle, as is indicated from the making procedure described above.

The composition of Formula 1, although its use is not restricted thereto, is especially useful as a cement or adhesive for attaching labels to bottles, metal cans and the like. It has the virtue of readily wetting a surface which is already wet with water (a common occurrence in the labeling of bottles) and yet, in the form of the final dried film, is not readily weakened by immersion in water, as are glue type adhesives. Labels attached to bottles with the cement of Formula 1 will remain tightly adhered thereto even after prolonged soaking in ice water or the like, which is a common occurrence in connection with the cooling or refrigeration of beverages such as beer, ginger ale and the like. Additionally the final dried film from the adhesive of Formula 1 is of such nature that labels joined to bottles therewith can be removed conveniently by soaking in a heated 5 per cent solution of sodium hydroxide in water.

It will thus be noted that this composition has an unusual combination of advantageous properties where characteristics are desired such as those needed in the case of label cements.

In addition to the properties mentioned above, the composition of Formula 1 possesses another characteristic which is highly important, for example, in the case of label cements or adhesives applied in a labeling machine such as the conventional automatic bottle labeling machines used in the soft drink and brewing industries. These machines generally operate on the principle of transferring adhesive from an adhesive reservoir by means of a rotating roll, to a second roll rotating in contact therewith and thence to contact arms which receive the adhesive from the second roll and transfer it to the label. This causes the adhesive to be wiped out or smeared in thin films under pressure. It is further desirable that the adhesive or dispersion be still "unbroken" after being applied on the label so that when the label is applied to the bottle, with pressure, the adhesive will spread out into a very thin film, which will then set very rapidly, due to absorption of water by the material of the label. For an adhesive to be useful under such severe conditions of application it must have, to a high degree, what might be termed pressure and spreading resistance; that is, the dispersion must not break during application on the labeling machine or equivalent. Many oil-in-water type dispersions have the tendency to "break" during the above type of application. In other words, the dispersed solids, when the dispersion breaks, assume the continuous phase and the resulting product loses its desired characteristics of spreadability. The composition of Formula 1 stands up very well under the severe test of repeated spreading and/or transfer in thin films without the dispersion breaking.

In the composition of Formula 1 it will be noted that there is a relatively large amount of plasticized polyvalent metal resinate and a relatively small amount of rubber, the rubber content of the latex being approximately 90 grams. The rubber content of the mix is, therefore, approximately 6.5 per cent that of the Zitro plasticized with mineral oil. It will also be noted that the polyvalent metal soap or zinc treated rosinate is present in several times the quantity of the alkali metal soap in the final dispersion.

The mixture of organic liquids, namely the isopropanol, n-butanol and ethyl acetate, have the function of minimizing or preventing gel structure in the finished dispersion adhesive. These materials improve or increase the flow characteristics of the dispersion for a given viscosity of the dispersion measured by dynamic methods. This characteristic is important, for example, in the case of the use of such adhesive in a labeling machine in that it will permit free circulation of the adhesive in the reservoir, as contrasted with channeling in the vicinity of the rotating roll. It may also be noted that viscosity is quite closely interrelated with the wet strength of the resulting adhesive.

The use of the mixture of organic liquids thus permits the use of a higher viscosity and there-

fore a higher wet strength while still maintaining adequate capacity to flow or circulate, e. g. in an adhesive reservoir, such as is used in automatic labeling machines.

Formula 2

	Grams
Pale Zitro	750
Mineral oil	625
WG rosin	125
Latex (60% solids)	150
Corn starch	42
50% KOH solution	39
Water	750

The composition of Formula 2 was formulated generally after the manner described above in connection with Formula 1. The Zitro and rosin were mixed together in an internal mixer, the mineral oil was then added thereto and then the latex was added, following which some water was added. The quantity of water added in this case prior to inversion was less than that described above in connection with Formula 1. When a smooth mix was attained, the KOH solution was added and then next the corn starch, in the form of a thick paste, was added, whereupon inversion of phase took place, the water becoming the continuous phase. Following this, additional quantities of water were gradually added to the mix to bring the same to desired viscosity.

The order of addition of the starch and potassium hydroxide may be reversed if desired, in which case inversion will take place upon addition of the potassium hydroxide.

Formula 3

	Grams
Pale Zitro	750
Mineral oil	625
WG rosin	125
Latex (60% solids)	150
50% KOH solution	47
Algin (sodium alginate etc.)	42
Water	1270

The making procedure for the composition of Formula 3, may for example, be generally the same as that above described in detail for Formula 1, except in the case of Formula 3 a larger amount of water may advantageously be employed in the composition prior to inversion. The water content prior to inversion may be, for example, about 1½ times that employed in connection with Formula 1 under similar conditions of operation.

Whereas casein is employed as the auxiliary dispersing agent and protective colloid of Formula 1, starch is used to provide this function in Formula 2 and align (which is a naturally occurring high molecular weight polysaccharide derivative) is employed for this same purpose in Formula 3. It will be noted that the methyl cellulose of Formula 1 was not actually employed in effecting the dispersion initially; however, it serves the function of a protective colloid and serves to improve the characteristics of the adhesive during application, for example to labels and the like. Methyl cellulose, or like material, has the further virtue of making it possible to produce an adhesive composition of desired viscosity, which has a lower proportion of rubber and polyvalent metal soaps, thus providing a finished composition having improved properties particularly in respect to spreading characteristics. By securing the desired stability and spreading characteristics of the dispersion adhesive by the use of methyl cellulose, as in Formula 1, instead of endeavoring to provide such stability by the use of increased amounts of casein, the resulting final dried film of cement also has greater water resistance, as is demonstrated during immersion of labeled containers for protracted periods in cold water.

Also, it is to be noted that the inversion of phase may be effected by adding methyl cellulose in lieu of casein, for example in the amount given in Formula 1. If this is done, an amount of casein such as that illustrated may be added subsequent to inversion, or not, as desired. The dispersion will be maintained in the absence of the addition of casein although a higher degree of stability is normally desired for use of the material in bottle labeling machines, or where comparable conditions are encountered, and ordinarily it is preferred either to add some casein subsequent to inversion, where none is added prior to inversion, or else to increase the quantity of methyl cellulose, or else add comparable amounts of another auxiliary dispersing agent such as herein otherwise illustrated.

Formula 4

	Grams
Lisor	500
Mineral oil	417
WG rosin	84
Latex (60% solids)	100
50% KOH solution	61
Casein	73
Water	1000

Formula 4 differs from Formulae 1 to 3, among other things, in that "Lisor" is used instead of "Zitro." Lisor is a limed rosin, composed principally of calcium rosinate, and has a metallic calcium content of approximately 5 per cent and an acid number of about 20 to 25.

A suitable method for compounding the composition of Formula 4 will be understood generally from the description given in connection with Formula 1 hereinabove. However it should be noted that a higher amount of water is needed in the case of Formula 4, which was inverted at about 120° F., than in the case of Formula 1, which was inverted at about 135° to 145° F. I employed approximately 2½ times as much water in the composition of Formula 4 prior to inversion, as compared with the amount used in connection with Formula 1.

Formula 5

	Grams
Lisor	500
Mineral oil	417
WG rosin	84
Latex (60% solids)	100
50% KOH solution	54
Corn starch	73
Water	1200

In terms of proportion, approximately twice as much water was used in the batch of Formula 5, prior to inversion, as was specified in the making procedure above described in connection with Formula 1. Also inversion was effected at a relatively low temperature, namely approximately 105° F. The resulting dispersion, how-

ever, appeared somewhat coarser but of comparable stability to the composition of Formula 4.

Formula 6

	Grams
Lisor	500
Mineral oil	417
WG rosin	84
Latex (60% solids)	100
Methyl cellulose	73
Water	1500

In this case the dispersion was inverted at a temperature of 130 to 140° F. The amount of water employed in the mix prior to inversion was 1000 grams which, proportionately, is approximately three times as much as employed in the composition of Formula 1.

It will be noted that no alkali hydroxide whatever was employed in producing the dispersion of Formula 6, methyl cellulose being the only dispersing agent employed. The composition of Formula 6 is nevertheless stable, in fact is still more stable than that of either Formula 4 or Formula 5, and is also more stable than that of Formula 7, given hereinafter.

Formula 7

	Grams
Lisor	500
Mineral oil	417
WG rosin	84
Latex (60% solids)	100
50% KOH solution	54
Algin	73
Water	1400

The algin employed was an alkaline material. The mineral oil employed, as in the case of other formulae given hereinabove, may be a petroleum oil which has a viscosity comparable to that of a lubricating oil of 40 to 50 S. A. E. viscosity, more or less, but which is relatively low in price as compared with that of lubricating oils. In cases in which color of the final product is important, the color of the mineral oil may be chosen so as to be relatively neutral in its effect on the color of the adhesive; at least so as not adversely to affect the color of the adhesive.

In each of Formulae 4, 5 and 7 the KOH solution was added following the addition of the auxiliary dispersing agents, i. e. casein, corn starch and algin respectively. Either approximately the quantity of alkali hydroxide specified in each of Formulae 4, 5 and 7, or else increased amounts of another dispersing agent, such as herein otherwise illustrated, should be added in order to accomplish the dispersion. The temperature at which inversion was effected, referring to Formula 7, was approximately 120° F.

All of the above formulae are useful, for example, as label cements. However the utility and workability of such compositions, particularly in automatic labeling machines, varies considerably and a composition such as that illustrated by Formula 1 is normally preferred.

The production of improved label adhesives and comparable adhesive compositions, as hereinabove indicated, involves only one aspect of the present invention. Adhesives having special utility for other purposes are also contemplated. The following formula illustrates an adhesive composition having special utility as a dry-seal adhesive, for example, in the sealing of envelopes, cardboard containers and the like.

Formula 8

	Grams
Red inner-tube reclaim	400
Pale Zitro	280
Mineral oil	120
Beta-naphthol	4
Tetrone A (dipentamethylene thiuram tetrasulfide)	4.4
Flectol H (condensation product of acetone and aniline)	8
Staybelite A1 (hydrogenated rosin)	80
Latex (60% solids)	800
Casein	46
KOH solution	33
Water	1250

A suitable method for compounding the above composition is as follows:

The reclaimed rubber is milled on a conventional rubber mill and then placed in a hot internal mixer (20–50 lbs./sq. in. gauge, steam pressure in the jacket). The pale Zitro and oil are fluxed together and then added slowly to the reclaim with continuous agitation. The beta-naphthol, Tetrone A, and Flectol H are then added, if desired, all at one time, followed by the addition of Staybelite A1 (hydrogenated rosin). The latex is then added gradually or as rapidly as it will be absorbed by the mixture and, when it is completely incorporated, about 225 grams of water are added. The casein dissolved in 138 grams of water and 5 grams of 50% KOH solution is slowly added with continuous agitation. The remainder of the 50% KOH solution is then introduced slowly, whereupon inversion of phase occurs. The inversion was effected at a temperature of about 190° to 200° F. Because of the high temperature employed or needed for inversion, the amount of water in the final dispersion will be somewhat less than the amount added, due to evaporation.

As contrasted with latex adhesives which have heretofore been suggested as dry-seal adhesives on envelopes and the like and which have the property of depositing films which will adhere well to each other but which have poor adhesion to paper, the composition of Formula 8 has decidedly superior adhesion to paper and the like in addition to the capacity of sealing to itself. Also the composition of Formula 8 has the virtue of substantially reduced materials cost as compared with latex adhesives heretofore employed.

The Tetrone A, which is capable of functioning as a vulcanization accelerator, when combined with the antioxidants, beta-naphthol and Flectol H, serves to improve further the ageing qualities of the dried film of the dry-seal adhesive. This mixture of materials is added to the internal mixer, as above noted, before the latex is added, and serves to minimize oxidation of the rubber of the latex throughout the addition of the latex and in the subsequent portion of the mixing operation.

The hydrogenated rosin (Staybelite A1) is employed to provide a substantially saturated soap-forming resin acid, which is relatively resistant to oxidation as compared with potassium oleate, or as compared with soaps produced from ordinary rosin, due to the unsaturated character of ordinary rosin and oleic acid.

This composition may be used for other purposes as well as for a dry-seal adhesive, as desired.

While the quantity of latex employed may be

varied considerably, the quantity given illustrates a useful proportion in order to produce an adhesive having good toughness, while still possessing other desired properties such as good aging, desired consistency, etc. Where desired, for example, to reduce the power load and facilitate inversion during the making of the composition of Formula 8, the quantity of latex employed may be reduced substantially, for example to the extent of 10 or 20 per cent or more, without any necessary change in the proportion of other ingredients, but with some reduction in the ability of the resulting adhesive to readily adhere, in the form of the final dried film, to another film of like nature.

The following formulae show other compositions especially adapted for other uses which are further illustrative of the present invention. Particularly, they illustrate various formulae having utility as tabbing cements (sometimes also referred to as padding cements), used to bind sheets together in pads of writing paper, scratch pads and the like.

Formula 9

	Grams
Light colored mechanically reclaimed tire carcass	475
Latex (60% solids)	40
Pale Zitro	400
Mineral oil	100
WG rosin	100
Latex (60% solids)	167
Casein	40
Sodium fluoride	2
50% KOH solution	40
Water	900

The tire carcass reclaim was made by grinding and masticating at an elevated temperature carcasses of passenger tires from which the tread had been removed. This material may be replaced, if desired, for example, by conventional tire carcass reclaims of commerce. The mechanically reclaimed tire carcass was milled on a rubber mill and 40 grams of the latex was added thereto during such milling operation. The latex served the advantage of making the reclaim more cohesive, thus aiding in the subsequent internal mixing operation by improving its workability. (By using commercial carcass reclaims, the step of adding latex during milling on a rubber mill may be eliminated.) The resulting milled reclaim composition is then transferred to an internal mixer, heated with about 20 pounds steam pressure, gauge, on the jacket, and mixing continued. A previously fluxed mixture of the "Zitro" and hydrocarbon oil is introduced, gradually to the mixer; then the WG rosin is added, after which the remaining 167 grams of latex is added gradually to the mixture, which is at a temperature below 210° F. Then the mixture is allowed to work until smooth, at which point 200 grams of water are added; if desired, all at one time. The casein is dissolved in a solution containing 120 grams of water, 2 grams of sodium fluoride and 4 grams of 50% KOH solution and this "solution" is added gradually to the mixture. The remainder of the 50% KOH solution is then introduced, whereupon inversion occurs. The inversion was effected at a temperature of 190 to 210° F. Under certain circumstances, for example where the mass being mixed is of sufficient size and the rate of cooling is suitably retarded, somewhat lower temperatures, e. g. of the order of 175° F., may be employed, although temperatures of the order of 190° F. or higher are common with a mix of the particular character of that of Formula 9.

The remaining water of Formula 9 may next be added to the batch, gradually or in increments, to bring the same to desired viscosity.

In the composition of Formula 9, it will be noted that the latex was added before inversion of phase of the dispersion.

Formula 10 illustrates a composition, having important utility, for example, as a tabbing cement, in which latex was added to the composition after inversion of phase, that is after the aqueous liquid made up the continuous phase of the dispersion.

Formula 10

	Grams
Gray tube reclaim	1050
Titanium dioxide	166
Brilliant red pigment (Imperial X1148)	138
Pale Zitro	138
Inner tube rubber heat degraded to liquid form	276
Beta-naphthol	3.3
Oleic acid	13.3
Glacial acetic acid	6.7
Polymerized trimethyl dihydroquinoline (Agerite resin D)	13.3
50% KOH solution	75.3
Casein solution	709
Water	1200
50% zinc dibutyl dithiocarbamate dispersion (Butyl Zimate)	13.3
75% Sulfur dispersion	10.3
Latex (75% solids)	444

The tube reclaim, titanium dioxide, Agerite Resin D and the brilliant red pigment (which is an insoluble organic pigment) were milled together on a rubber mill. When suitably plasticized or softened, this composition was placed in an internal mixer, heated by steam at 20 to 50 pounds per square inch, gauge, in the jacket, and mixing or agitation was continuously carried on. Then the pale Zitro and tube rubber, heat degraded to liquid form, were melted together and added as a warm semi-solid mixture to the batch in the internal mixer. Agitation was then continued until a smooth mixture was obtained, following which the beta-naphthol, oleic acid and glacial acetic acid, the latter being dissolved in an equal quantity of water, were added, preferably individually and successively. Then approximately 340 grams of water and/or ice were added, the proportion of ice being sufficient to reduce the temperature of the mass so as to bring the same within the range of 130° to 160° F., preferably about 150° F. Then approximately half of the KOH solution was added, gradually, followed by approximately half the casein solution. After which the remainder of the KOH solution is added. Inversion of phase will now take place upon continuing the mechanical working for some time, e. g. about 10 to 30 minutes. When inversion is completed, this is obvious upon inspection. Then the dispersion is gradually diluted with water, amounting to about 200 grams less than the total to be added, while continuing mechanical mixing. Then there is successively added the butyl zimate dispersion, the sulfur dispersion, the remaining half of the casein solution and the latex. Each of the last mentioned ingredients are added gradually, particularly the casein solution and the latex. Gradual addition of the casein solution is de-

sirable so as to avoid the possibility of localized thickening or, under certain circumstances, localized reinversion of phase.

The 709 grams of casein solution of Formula 10 was composed of 117 grams of casein, 12 grams of 50% KOH solution and 580 grams of water.

Gradual addition of the latex and also addition of the same while maintaining the batch at a suitably low temperature, e. g. at about 115° F. or somewhat less, are desirable to avoid reinversion of phase, or setting up of the batch in the mixer. Next the remaining 200 grams of water may be gradually added, or more or less water may be added to control the consistency of the adhesive as desired.

The addition of latex prior to inversion, as in the composition or Formula 9, has the virtue of providing an adhesive having increased tensile strength, greater adhesiveness and more elongation at break (i. e. more elasticity) in the form of the final dried film, for a given amount of latex used, than in the case where the latex is added subsequent to inversion of phase. However, the problem of making may be complicated by addition of all the latex prior to inversion, i. e. the batch may become so tough when the latex, or all of the latex, is added prior to inversion that it becomes impossible satisfactorily to work it in the mixer. It may thus be desirable to withhold part of the latex and add it after inversion. Where only small amounts of latex are employed, usually it is preferable to add all of the latex prior to inversion; whereas where relatively large amounts of latex are to be employed, at least a portion of the latex may often be added subsequent to inversion so as to simplify the mixing problem.

The following two formulae, which also may be used as tabbing cements, or for other adhesive purposes, illustrate adhesive compositions made without the use of latex.

Formula 11

Red tube reclaim	grams	1200
Lisor	do	300
Casein	do	50
Ester gum	do	100
Oleic acid	do	48
Solid KOH	do	27
Conc. NH_3 solution	cc	25
Water	cc	1175

In making up the composition of Formula 11, the red tube reclaim was first milled on a rubber mill to render the same plastic and then the plastic mass was placed in an internal mixer, heated by jacket steam at 20 to 50 pounds per square inch gauge. Then the 'Lisor" (lime treated rosin) was added gradually, e. g. in a plurality of increments. When a smooth batch is obtained, the casein in dry state (or in the form of a "solution" if desired) may be added, all at once if desired. Next the ester gum and oleic acid are added successively and in increments, while continuing the mixing. Next about 450 grams of water and/or ice are added to reduce the temperature of the batch to a temperature within the range of 130 to 160° F., e. g. to about 150° F. Then the KOH dissolved in an equal quantity of water is added gradually, followed by the ammonia solution. Inversion of phase may take place immediately following the addition of the KOH or else upon the addition of the ammonia solution, depending upon the size of the batch, particular character of the batch and the exact temperature employed. Next, after continuing the mixing until a smooth uniform batch is obtained, the remainder of the water may be added, or more or less water may be added, to control the viscosity of the batch within the range desired.

Formula 12

	Pounds
Gray tube reclaim	167
Titanium dioxide	21
Brilliant red pigment	17.5
Glacial acetic acid	0.84
B-naphthol	0.2
Polymerized trimethyl-dihydro quinoline (Agerite resin D)	1.16
Pale Zitro	20.0
Oleic acid	1.67
Casein	8.4
Solid KOH	4.9
50% zinc dibutyl dithiocarbamate dispersion (Butyl Zimate)	1.67
75% sulfur dispersion	1.25
Water	212.0

A suitable method of compounding the composition of Formula 12 is very similar to that described above in connection with Formula 10. The gray tube reclaim, titanium dioxide, "Agerite resin D" and the red pigment were milled together on a rubber mill until a uniform plastic mass was obtained. This was then placed in an internal mixer (jacket steam pressure about 100 pounds per square inch gauge) and then the "Zitro" was added gradually, with continuous agitation. Following the addition of all the Zitro and when a smooth batch is obtained, the beta naphthol and oleic acid are added successively, or together, if desired. Next the glacial acetic acid, dissolved in an approximately equal quantity of water, may be added, commonly as a single increment. Next approximately 45 pounds of water and/or ice may be added, the proportion of ice being controlled in order to bring the temperature of the resulting batch within the range of 130° to 160° F., e. g. about 150° F. Then approximately half of the KOH dissolved in an equal quantity of water is added gradually, followed by the addition of the casein dissolved in an alkaline solution containing about 40 pounds of water and about 0.85 pounds of KOH. Then the remainder of the KOH solution is added, whereupon inversion occurs, followed by the attainment of a smaller particle size upon working for 15 to 30 minutes. Then the butyl zimate dispersion and sulfur dispersion are added, usually at the same time and usually in a single increment. After mixing is continued to get a uniform batch, the remainder of the water is then added gradually, or more or less water is added, to bring the batch to the final viscosity or consistency desired.

The glacial acetic acid serves the helpful function, especially where reclaimed rubbers are employed which contain a substantial amount of soap, of making it easier to work water into the batch and to disperse the same uniformly through the rubbery composition prior to inversion.

In the case of the composition of Formula 12, the proportion of alkali added is sufficient so that the pH of the final mass is substantially above 7, e. g. of the order of 11.

In general the compositions of Formulas 9, 10, 11 and 12, had a somewhat higher pH than the other formulae. The composition of Formula 1

ordinarily has a pH of the general order of 9, usually in the range of 9 to 9.5, or of that order. However, in the compositions of Formulae 4, 5, and 7, the pH was higher than that of Formula 1. On the other hand the composition of Formula 6 had a pH somewhat lower than that of Formula 1, i. e. of the general order of 7, or between 7 and 8.

It is to be observed that a novel method of incorporating rubber into compositions of the type herein defined is involved in the formulation of various of the compositions above illustrated, for example, is involved in the formulation of the adhesives of Formulae 1 to 9 inclusive. However the broader phases of this method of incorporating rubber into compositions of the types herein involved, as well as in other types of compositions or dispersions, are being claimed in a separate application.

Compositions such as defined in Formulae 9, 10, 11 and 12, of which the compositions of Formulae 9 and 10 are preferred, have special advantages over glue and modified glue compositions heretofore employed as tabbing adhesives. For example, the compositions herein defined may be applied cold whereas glue must be applied hot; they provide flexible films, whereas glue is brittle; they are not subject to being eaten by mice or by termites or the like, whereas glue, which is a protein, provides a problem in this respect during storage of paper pads and the like.

As compared with latex which has been heretofore employed to form adhesives used as tabbing cements, the compositions of the present invention, for example those illustrated by Formulae 9 to 12, have the advantage of lower cost and also are substantially free from odor. The compositions of Formulae 10, 11 and 12 are practically odorless. Also the compositions of the present invention have better aging qualities than ordinary latex, for example, with respect to the absence of a semi-liquid stage during atmospheric oxidation, which is characteristic of adhesive films heretofore produced from crude rubber.

It will be noted that each of the specific formulae given hereinabove involve the use of polyvalent metal soaps or resinates in water dispersed compositions or adhesives, although some alkali metal soap is employed in most of the dispersions above illustrated. Where the alkali metal soap is employed, it will be noted that its quantity is substantially less than that of the polyvalent metal soap and ordinarily, according to preferred aspects of the present invention, the proportions of the alkali metal soap is less than ½ and even less than ⅓ of that of the polyvalent metal soaps or resinates, such as zinc and/or calcium abietate. For example, in the composition of Formula 1, the polyvalent metal soap is present to the extent of approximately 5 times that of the alkali metal soap. While I contemplate water dispersions or adhesives of the oil-in-water type in which alkali metal soaps are restricted to minor amount in comparison with polyvalent metal resinates, or where the alkali metal soaps (especially alkali metal soaps of aliphatic acids such as oleic acid) are substantially absent, I also contemplate compositions of the general type just defined which contain a substantial amount of rubber in the dispersed phase. I also contemplate as a part of my invention the final dried film of adhesive or elastic material resulting from such dispersions. In my more preferred compositions, where rubber is employed, the rubber is ordinarily present to the extent anywhere within the range of 0 to 1000 per cent of the weight of the polyvalent metal soap, but commonly within the range of 6 to 100 per cent where, for example, an undegraded form of rubber is employed, or, for example, up to about eight or more times as much rubber as polyvalent metal soap where reclaim is used. Where relatively small amounts of rubber are employed, as above indicated, it is advantageous to introduce the rubber into the batch, for example, in the manner described in connection with Formula 1. In other types of adhesives and where varying properties are desired, larger amounts of rubber, for example either in the form of crude or reclaimed rubber or synthetic rubber-like materials or elastomers, may be introduced, e. g. in the manner described in connection with Formula 12. Exemplary of synthetic rubber-like materials contemplated are isobutylene polymers of high molecular weights, such as Vistanex, but other synthetic rubber-like materials or compositions which are compatible with my polyvalent metal resinate composition are contemplated.

While the polyvalent metal soaps which I prefer to employ have been particularly illustrated by zinc and/or calcium resinates, or by zinc and/or calcium abietate, other polyvalent metal resinates are contemplated although, all things considered, the zinc and/or calcium resinates are commonly preferred. For example, magnesium resinates furnish a useful function and may be employed in adhesive compositions, but these materials are not available commercially at the present time. Likewise barium, lead or aluminum resinates may be employed under suitable conditions, where desired, but are less preferred at the present time, all things considered, than the zinc and/or calcium resinates hereinabove specifically illustrated.

Polyvalent metal resinates, as herein illustrated, when used as modifiers for rubber, produce dispersions which, in the form of the final dried film, are stronger than are compositions where, for example, ester gum, cumar resins and the like are used with the rubber to the exclusion of polyvalent metal resinates.

While I illustrated the preparation of my dispersions especially by first producing a water-in-oil type dispersion and then inverting the dispersion, I have also produced dispersions without going through the step of inversion. For example a thick casein paste was prepared, to which was added latex and additional water, retaining the thick paste-like character. To this paste, e. g. in an internal mixer, was added slowly a molten mixture of mineral oil and the polyvalent metal resinate, alternately with increments of water. When a smooth batch is attained, the dispersion may be diluted as desired with further amounts of water. However, this is not as advantageous as the inversion method of formulation.

The above descriptions and examples are intended to illustrate and not to limit the scope of the present invention.

What I claim is:

1. An oil-in-water type dispersion wherein individual dispersed particles each comprise an intimate blend of a polyvalent metal soap and rubber, and are dispersed in an aqueous vehicle.

2. A stable adhesive dispersion comprising an adhesive material comprising a substantially uniform blend of a polyvalent metal resinate and undegraded rubber, added in the form of

latex, dispersed in an aqueous vehicle, said rubber being present in lesser proportion than said polyvalent metal resinate.

3. An adhesive dispersion of the oil-in-water type comprising a substantially uniform blend of a polyvalent metal resinate and a compatible organic elastomer, dispersed in an alkaline aqueous vehicle containing a hydrophilic organ colloid, which latter is capable of repressing the tendency of the polyvalent metal resinate to re-invert the dispersion.

4. An adhesive dispersion of the oil-in-water type including discrete particles each of which comprises a substantially homogeneous blend of a polyvalent metal resinate and a compatible high molecular weight rubberlike organic elastomer, dispersed in a vehicle having a pH greater than 7, and a hydrophilic organic protein colloid.

5. An adhesive dispersion of the oil-in-water type comprising an adhesive material containing a substantially uniform blend of a bi-valent metal resinate with a different but substantially compatible rubberlike organic elastomer of high molecular weight, dispersed in an alkaline aqueous vehicle, and a hydrophilic organic protective colloid comprising a hydrophilic proteinaceous colloid, and an alkali metal soap, present as primary dispersing agent, in minor proportions by weight in relation to said bi-valent metal resinate.

6. An oil-in-water type dispersion comprising a blend of a polyvalent metal soap and rubber dispersed in an aqueous vehicle containing a hydrophilic soap dispersing agent and a hydrophilic proteinaceous organic colloid.

7. An oil-in-water type dispersion comprising an intimate blend of a polyvalent metal soap and rubber dispersed in an aqueous vehicle containing a hydrophilic soap dispersing agent and a hydrophilic colloidal polysaccharide compound.

8. An oil-in-water type dispersion comprising a blend of a polyvalent metal soap and rubber dispersed in an aqueous vehicle containing a hydrophilic organic colloid, said polyvalent metal soap being present in greater proportion by weight than said hydrophilic organic colloid.

9. An oil-in-water type dispersion including individual dispersed particles each of which comprises a substantially homogeneous blend of a polyvalent metal soap and rubber dispersed in an aqueous vehicle containing a hydrophilic organic colloid, said polyvalent metal soap being present to the extent by weight of at least twice that of said hydrophilic organic colloid.

10. An oil-in-water type dispersion comprising a substantially uniform blend of a polyvalent metal soap and rubber dispersed in an aqueous vehicle containing a hydrophilic soap dispersing agent, a hydrophilic proteinaceous colloid, and a hydrophilic colloidal polysaccharide.

11. An oil-in-water type dispersion comprising an intimate blend of a polyvalent metal soap and rubber dispersed in an aqueous vehicle containing a hydrophilic soap dispersing agent, a hydrophilic proteinaceous colloid, and a hydrophilic polysaccharide colloid, said polyvalent metal soap being present to the extent by weight of at least twice that of the aggregate of said hydrophilic soap dispersing agent, said protein or derivative and said polysaccharide.

12. An adhesive dispersion of the oil-in-water type comprising a substantially uniform blend of a polyvalent metal resinate and a compatible, high molecular weight rubberlike organic elastomer, dispersed in a vehicle having a pH greater than 7, and a hydrophilic colloidal high molecular weight polysaccharide.

13. An adhesive dispersion of the oil-in-water type comprising an adhesive material containing a substantially uniform blend of a bi-valent metal resinate with a different and rubberlike organic elastomer of high molecular weight, dispersed in an alkaline aqueous vehicle, and a hydrophilic organic protective colloid comprising a high molecular weight polysaccharide compound, and a hydrophilic soap dispersing agent, present as primary dispersing agent, in minor proportion by weight in relation to said bi-valent metal resinate.

14. An adhesive dispersion of the oil-in-water type comprising an adhesive material containing discrete particles including a substantially uniform blend of a bivalent metal resinate and rubber, said particles being dispersed in an aqueous vehicle, and a hydrophilic organic protective colloid comprising a hydrophilic colloidal high molecular weight polysaccharide compound.

15. An adhesive dispersion of the oil-in-water type comprising a dispersed adhesive material including discrete particles each of which comprises a substantially uniform blend of a bivalent metal resinate and rubber, said particles being dispersed in an aqueous vehicle containing a hydrophilic protein colloid.

16. An adhesive dispersion of the oil-in-water type in which the particles of dispersed material are composed to substantial extent of a polyvalent metal soap of a cyclo-aliphatic acid, uniformly intermixed and blended with a compatible rubberlike organic elastomer, and the continuous phase of the dispersion contains a quantity of alkali metal soap at least in small amount but not to a greater extent by weight than 50% of that of said polyvalent metal soap.

17. An oil-in-water type dispersion comprising particles containing a substantially uniform blend of rubber and a polyvalent metal soap of a rosin acid, dispersed in an aqueous vehicle containing a hydrophilic organic colloid, which latter is capable of repressing the tendency of the polyvalent metal rosinate to re-invert the dispersion.

18. An adhesive dispersion of the oil-in-water type comprising a substantially homogeneous blend of rubber and a polyvalent metal resinate dispersed in an alkaline aqueous vehicle containing a hydrophilic organic colloid, which latter is capable of repressing the tendency of the polyvalent metal resinate to re-invert the dispersion.

19. A bottle label adhesive of the dispersion type having particles composed of an adhesive composition comprising a substantially uniform blend of zinc and calcium rosinates, mineral oil plasticizer and substantially undegraded rubber, said particles being dispersed in an aqueous vehicle containing a hydrophilic organic colloid, which latter is capable of repressing the tendency of the polyvalent metal rosinates to re-invert the dispersion.

20. An adhesive of the dispersion type having utility as a tabbing cement which comprises an adhesive composition comprising particles including a substantially uniform blend of reclaimed rubber, undegraded rubber and a bivalent metal resinate, said particles being dispersed in an aqueous vehicle containing a hydrophilic organic colloid, which latter is capable of repressing the tendency of the bi-valent metal resinate to re-invert the dispersion.

21. In the production of a dispersion of the oil-

in-water type which upon application as a film and loss of a portion of its water yields a tacky adhesive film, the steps which include mixing rubber and a polyvalent metal soap to provide a substantially homogeneous blend thereof and disseminating a restricted amount of water therein to provide a uniform dispersion of the water-in-oil type and of viscous consistency, and thereafter effecting inversion of phase thereof to yield an oil-in-water type dispersion, and adding water thereto, with mixing, to control the viscosity of the finished oil-in-water type dispersion as desired.

22. The process of producing dispersions of the oil-in-water type which comprises mixing a polyvalent metal resinate, latex and a restricted amount of water together in an internal mixer at superatmospheric temperatures, thereby to produce a dispersion of water in the resinous composition, then effecting inversion of phase of the dispersion and stabilizing the resulting oil-in-water type dispersion by the use of an alkali metal dispersing agent and a hydrophilic organic colloid, which latter is capable of repressing the tendency of the polyvalent metal resinate to re-invert the dispersion, the mass at the time of inversion being maintained within a restricted range of temperatures, above room temperatures and below 210° F.

23. The process of producing dispersions of the oil-in-water type which comprises mixing a polyvalent metal resinate and rubber, together with a restricted amount of water to produce a uniform blend of said polyvalent metal resinate and said rubber and to provide a dispersion of said water in said blend, then effecting inversion of phase of the dispersion and stabilizing the resulting oil-in-water type dispersion by the use of an alkali metal dispersing agent and a hydrophilic organic colloid, which latter is capable of repressing the tendency of the polyvalent metal resinate to re-invert the dispersion, the mass at the time of inversion being maintained within a restricted range of temperatures, said range lying above ordinary room temperatures and below 210° F.

24. The process of producing dispersions of the oil-in-water type which comprises blending a polyvalent metal soap and rubber to provide a substantially homogeneous blend and uniformly disseminating a restricted amount of water therein to provide a water-in-oil dispersion of viscous consistency, and effecting inversion of phase of said water-in-oil dispersion to yield the desired oil-in-water type dispersion, a dispersing agent including a hydrophilic organic colloid capable of counteracting the tendency of the polyvalent metal soap to re-invert the dispersion being introduced into the batch prior to the said inversion.

25. The process of producing a dispersion of the oil-in-water type, which upon application as a film to a surface and loss of part of its water yields a tacky adhesive film, comprising mixing rubber and a polyvalent metal soap to provide a substantially homogeneous blend thereof and mixing a restricted amount of water therein to provide a uniform dispersion of the water-in-oil type and of stiff, viscous consistency, and thereafter effecting inversion of phase of said water-in-oil dispersion to yield an oil-in-water type dispersion, a dispersing agent including a hydrophilic organic colloid capable of repressing the tendency of the polyvalent metal soap to re-invert the dispersion being introduced into the batch prior to the time that the said inversion is effected, the mass at the time of inversion being maintained within a restricted range of temperatures, above room temperatures and below 210° F.

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