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SIZING COMPOSITIONS AND METHOD OF USING THE SAME

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This invention relates to the sizing of various materials such as fibers, pulps, textiles, and the like, and it is particularly directed to the provision of a new sizing composition wherein the conventional rosin component is replaced by cyclic compounds of petroleum origin. Since this size is especially adapted for employment in the beater-sizing of paper-making stock preparatory to sheeting the stock on a paper-making machine, the invention will be particularly described hereinafter as it relates to the paper-making art even though the size is useful for other purposes as well.

The majority of the sizing compositions which are presently employed in paper-making mills contain a substantial portion of rosin (colophony). Due to the high cost and limited availability of this material, a great deal of work has been done in an effort to provide a satisfactory and inexpensive rosin substitute. The cyclic, predominantly aromatic compounds obtained as by-products in the refining of the petroleum oils have been tested for this purpose by a number of workers. As a result of this work it has been shown that as the petroleum portion replaces more than about 25% of the rosin in the sizing composition, difficulty is encountered in that the sized fibers tend to stick to the rolls of the press and soon cause rupture of the sheet material being passed through the press (see The Paper Maker, London, England, International Number (1946), pp. 24–30).

In view of the low cost and plentiful supply of the cyclic compounds separated from petroleum during the various refining operations, it would be desirable if satisfactory sizing compositions were available wherein such compounds might replace the rosin either entirely or at least in major part, and it forms an object of the present invention to provide a sizing composition of this character. A further object is to provide a sizing composition which will not induce the sticking of fibers to the press rolls and which will otherwise have the desirable characteristics of conventional rosin sizes. The nature of other objects of the invention will be apparent from a consideration of the descriptive portion to follow.

It has now been discovered that the acid-free cyclic components removed from petroleum oils during the refining thereof can be used as a size without the necessary addition of rosin provided the sizing composition contains a special type of paraffin wax having an exceptionally high melting point, in addition to the emulsifying agent which is normally present in compositions of this character. This sizing composition can be used in any desired concentration without causing sticking, or pitch difficulties, and in general possesses all the desirable attributes and performance characteristics of conventional rosin sizes while being much less expensive than the latter.

The petroleum fractions employed as the size are essentially acid-free and are predominantly made up of aromatic and naphthenic hydrocarbons, though small amounts of cyclic compounds may be present which contain sulfur or nitrogen in the molecular structure. In addition, they usually contain from about 2 to 25% of neutral petroleum oils which are essentially paraffinic in character. However, since these paraffinic components are never present in major amount, the size will be referred to herein as a cyclic petroleum component, or fraction. Included among these cyclic components are the various residual asphalts as well as the extracts obtained by treating the oil, or fractions thereof, with one or more polar solvents such as liquid sulfur dioxide,

phenol, cresol, furfural, propane, beta,beta-dichloroethyl ether, nitrobenzene and the like, as described, for example, in U. S. Patents Nos. 2,023,375, 2,357,344, 2,360,859 and 2,356,898. Combinations of solvents, as phenol with cresylic acid, or liquid sulfur dioxide with benzene or toluene are useful, and desirable extracts are also obtained by treating the petroleum fraction with mutually immiscible solvents such as cresylic acid and propane. Methods of this type which may be used are described, for example, in U. S. Patents Nos. 2,029,190, 2,124,602 and 2,322,083. The various petroleum residues and extracts which remain on distilling off the solvent or solvents employed vary in viscosity from about 10 cs. at 210° F. up to more or less solid asphaltic compositions softening at about 100° F. to 200° F., and in specific gravity (d 20/4) from about 0.9 to 1.05. Their initial boiling point is at least 300° F. at 1 mm. Hg. These various cyclic petroleum components, which may be used either singly or in any desired admixture, normally constitute from about 30 to 85% by weight of the sizing composition.

The wax component of the sizing composition, which should be present in an amount of from about 5% to 40% by weight of the composition, is one having a melting point of at least 155° F. which contains at least 55% straight chain (paraffinic) hydrocarbons. Preferably the wax has a melting point of at least 160° F. and contains at least 80% of the straight chain hydrocarbons. Waxes of this character are obtained from a number of different crudes, including Netherlands East Indies oils and as well as from those obtained near Ventura, California, for example. They differ from conventional paraffin waxes in having an appreciably longer chain length as evidenced by their unusually high melting points and other physical and chemical characteristics. A petroleum wax which has proven to be highly satisfactory for use in the sizing compositions described herein is sold by Union Oil Company under the trade name of "Aristowax," M. P. 160–165° F. In general, the lower the content of the straight chain component in the wax, the higher the melting point should be. Thus, while using waxes which contain but about 55% of straight chain components, the best results have been obtained with those waxes of this character which melt at or above 170° F. On the other hand, good results have been obtained with waxes melting at about 155° F. in the case of waxes containing 90% or more of straight chain components.

The third component of the sizing composition comprises an emulsifying agent which is present in an amount of from about 5% to 40%, based on the total weight of the size composition. A wide variety of emulsifying agents can be employed, including sodium oleate, ammonium oleate, sodium stearate, sodium naphthenate, potassium oleate, triethanolamine oleate, tall oil and rosin. In many cases the emulsifying agent can be formed in situ in the cyclic petroleum component, preferably after the wax is added thereto. Thus, for example, in the case of the naphthenate sizes, a naphthenic acid or a mixture of naphthenic acids can be added to the size (or to a size-wax melt) with warming if necessary to insure uniform distribution, following which there is added an amount of an aqueous solution of an alkaline agent sufficient to substantially neutralize the naphthenic acids present. A wide variety of different alkaline agents are useful for this purpose, including sodium hydroxide, potassium hydroxide, ammonium hydroxide, and sodium carbonate, as well as amines such as dimethylamine, propylamine, cyclohexylamine or ethanolamine.

While the sizing compositions described herein are highly effective even when no rosin whatsoever is employed in the composition, rosin can be used to replace any desired proportion up to 50% of the petroleum-derived sizing ingredient. Again, other materials, as hydrocarbon oils or conventional paraffin waxes, for example, can also be present in minor amount.

Once the sizing composition has been prepared, it is preferably combined with a quantity of water over and above any employed in adding any alkaline agent, thereby forming either an oil-in-water or a water-in-oil emulsion. The latter can be stored until needed and then

readily diluted at the paper mill without inducing phase separation or loss in sizing power, thereby forming dilute emulsions of the oil-in-water type which are similar in character and properties to the conventional rosin emulsion sizes. The emulsions of the invention can be added to the pulp in the beater engine at any stage of beating. The sizing may also be carried out in the Jordan machine or at the screens. The amount of size required for a given application is somewhat dependent on the nature of the fibrous material being treated as well as the method and conditions of treatment. However, as little as 0.2% of the sizing composition, based on the dry weight of the pulp, is effective, though up to 10% or more can be used. A preferred range is from about 0.5 to 5%.

A wide variety of precipitants can be used to fix the sizing composition on the fibers. Alum, aluminum sulfate, calcium chloride, sulfuric acid or hydrochloric acid are all suitable for this purpose, but by paper-makers alum is preferred. The precipitant can be added to the pulp furnish along with the size, though generally it is preferred to add the precipitant sufficiently later in the process so as to provide time for uniform distribution of the size before the precipitant is introduced.

The sizes of the invention can be used in making papers filled with kaolin and the like as well as in making unfilled papers. Further, these sizes do not cause difficulties on applying paper inks or dye stuffs to the finished paper.

The following examples illustrate the invention in various of its application.

Example I

In this operation the petroleum material employed consisted of so-called "naphthenate bottoms" which served not only as the size, but also as the emulsifying agent. The term "naphthenate bottoms" designates the material obtained by introducing a petroleum oil fraction, previously topped to remove the gasoline and other light fractions, into a fractionating column below a tray which is continuously supplied with caustic, the feed vapors coming into contact with the caustic solution which is present on the tray. The caustic reacts with the naphthenic acids present in the feed, converting the same to naphthenates, while at the same time the solution selectively extracts various of the cyclic compounds which are present in the feed along with minor amounts of paraffinic hydrocarbons. The naphthenic bottoms product is continuously drawn off from the caustic-containing tray. In the present operation the naphthenic bottoms employed contained about 70% petroleum components (predominantly cyclic in character) together with about 30% sodium naphthenates, as formed in the tray solution, which act as the emulsifying agent when the naphthenate bottoms are employed in sizing compositions. This naphthenate bottoms product is a highly viscous, semi-solid material at room temperatures. The non-naphthenate fraction of the naphthenate bottoms had a sp. gr. (*d* 20/4) of 0.995, a mixed aniline point of 58.1° C. and a molecular weight of 918. This fraction contained about 1% each of sulfur and nitrogen.

The sizing composition was prepared by dissolving 15% by weight (in terms of the weight of naphthenate bottoms) of a paraffin wax melting at 160 to 165° F. and having approximately 80% straight chain molecular components (Aristowax, marketed by Union Oil Company) in the foregoing naphthenate bottoms at a temperature of about 125° C. The product was then cooled to a temperature slightly below 100° C. and was then added to water in an amount sufficient to provide a 10% emulsion of the oil-in-water type. The size emulsion was then stored for a period of several days, following which it was diluted with water to provide a 1% oil-in-water emulsion which was then added to kraft beaten pulp in an amount sufficient to provide a pulp mixture containing 2.5% by weight size based on the weight of the dry pulp. The sized pulp was stirred for a period of 15 minutes, after which 3% of papermakers alum (based on the dry weight of pulp) was added to precipitate the size. Stirring was continued for another 15 minutes, after which time the pulp was formed into sheets having a thickness of about 0.006 in. on a cylinder type paper making machine having a cylinder width of 18 in. and equipped with a single press section and a Yankee drier. The water resistance of the resulting dry paper was tested by the TAPPI Dry Indicator Method No. T433m–44, a test which measures the length of time required for water to penetrate the paper as indicated by a change in color of a dry, sugar-fuchsin indicator placed on the dry side of the paper. In this test, wherein a time of about 25 seconds is indicative of good water resistance, it was found that the paper sized in accordance with the process here described had a time of 36 seconds. In this operation the paper making unit was maintained in continuous operation for a period of three hours. During this period the upper roll of the press section remained free of attached fibers, thereby indicating that the size would not induce sticking, or pitch troubles.

In a companion operation conducted in the same manner, but without adding any wax to the naphthenate bottoms, the pulp rapidly began to build up on the upper roll of the press section until, after a period of 20 minutes, the sheet ruptured and necessitated discontinuance of the operation. Similar difficulties were encountered when, in lieu of the Aristowax, there was employed 15% of a paraffin wax melting at 122–124° F. and containing over 90% straight chain components, the sheet here rupturing in about 35 minutes. Again, the sheet also ruptured in a period of 35 minutes when there was employed 15% of a paraffin wax melting at about 160° F. and containing 40% of straight chain components.

Example II

This operation was conducted under the same conditions as described in Example I above, in the second paragraph, except that in place of 15% Aristowax there was employed 30% of a wax melting at about 170° F. and containing 55% of straight chain hydrocarbons. At the end of three hours of continuous operation there was no evidence of any sticking of the fibers to the upper press roll. The dried paper prepared with this high-wax size composition had good resistance to penetration by water as indicated by a time of 37 seconds as measured by the TAPPI Method described in Example I.

Example III

In this operation there was employed as the size a material obtained by extracting a lubricating oil distillate with furfural, the furfural being distilled from the extract before the latter was employed in compounding the size compositions. This extract was heated to about 125° F. and blended with 15% Aristowax (M. P. 160–165° F.), based on the total weight of the non-aqueous size composition. To the resulting melt was then added 5% tall oil, again based on the total dry weight of the composition. The resulting water-in-oil emulsion was mixed with moderate agitation for 15 minutes, following which the emulsion was inverted by addition of water to form a 50% oil-in-water emulsion. The latter emulsion was then diluted to form a 1% oil-in-water emulsion which was added to kraft pulp in an amount sufficient to provide 2.5% size based on the dry weight of pulp. On being stirred for a period of about 15 minutes, the size was precipitated by the addition of 3% paper-makers alum and the sized pulp was then formed into sheets in the same fashion as described in Example I. The dry sheets, when tested by the TAPPI Dry Indicator Method, withstood water penetration for a period of 32 seconds. This paper making operation was continuously practiced for a period of 70 minutes, and at the end of this time there was no evidence of any sticking of the pulp to the upper roll of the press section.

On the other hand, when the same size composition was employed, but without the addition of any wax, sticking of the pulp to the roll quickly ensued and the sheet ruptured after a period of only 15 minutes.

The invention claimed is:

1. In a process of sizing fibrous materials wherein size particles are precipitated on said materials from an aqueous emulsion, the improvement which comprises using as the size a mixture of emulsifier and cyclic petroleum components in the proportions of 5 to 40 parts of said emulsifier to 30 to 85 parts of cyclic petroleum components, said cyclic petroleum components having a viscosity varying from about 10 cs. at 210° F. up to solid compositions softening at about 200° F., an initial boiling point of at least 300° F. at 1 mm. pressure of mercury, and a specific gravity (*d* 20/4) of 0.9 to 1.05 and containing not more than 25% of paraffin oil, together with from about 5 to 40%, in terms of the weight of the non-aqueous portion of the emulsion, of paraffin wax having

a melting point of 155° F. to about 170° F. and containing at least 55% straight chain hydrocarbons.

2. In a process of sizing fibrous materials wherein size particles are precipitated on said materials from an emulsion in water, the improvement which comprises using as the size a mixture of naphthenate bottoms containing sodium naphthenates and cyclic petroleum components in the proportions of 5 to 40 parts of sodium naphthenate to 30 to 85 parts of cyclic petroleum components, said cyclic petroleum components having a viscosity varying from about 10 cs. at 210° F. up to solid compositions softening at about 200° F., an initial boiling point of at least 300° F. at 1 mm. pressure of mercury, and a specific gravity (*d* 20/4) of from 0.9 to 1.05 and containing not more than 25% of paraffin oil together with from about 5 to 40%, in terms of the weight of the non-aqueous portion of the emulsion, of paraffin wax having a melting point of 155° F. to about 170° F. and containing at least 55% straight chain hydrocarbons.

3. A water-oil emulsion containing, as the non-aqueous component, from about 5 to 40% of sodium naphthenate emulsifying agent, from about 5 to 40% of paraffin wax having a melting point of 155° F. to about 170° F. and containing at least 55% straight chain hydrocarbons, and from about 30 to 85% of a mixture of cyclic petroleum components having a viscosity of at least 10 cs. at 210° F. up to solid compositions softening at about 200° F., an initial boiling point of at least 300° F. at 1 mm. pressure of mercury, and a specific gravity (*d* 20/4) of from 0.9 to 1.05 and containing not more than 25% of paraffin oil.

4. A water-oil emulsion containing, as the non-aqueous component, from 60 to 95% of naphthenate bottoms containing sodium naphthenates and cyclic petroleum components in the proportions of 5 to 40 parts of sodium naphthenate to 30 to 85 parts of cyclic petroleum components, said cyclic petroleum components having a viscosity varying from about 10 cs. at 210° F. up to solid compositions softening at about 200° F., an initial boiling point of at least 300° F. at 1 mm. pressure of mercury, and a specific gravity (*d* 20/4) of from 0.9 to 1.05 and containing not more than 25% of paraffin oil and from about 5 to 40% of a paraffin wax having a melting point of 155° F. to about 170° F. and containing at least 55% straight chain hydrocarbons.

5. A composition consisting essentially of about 30 to 85 parts of a cyclic petroleum fraction predominantly made up of aromatic and naphthenic hydrocarbons and having a viscosity of at least 10 cs. at 210° F. up to solid compositions softening at about 200° F., an initial boiling point of at least 300° F. at 1 mm. pressure of mercury, and a specific gravity (*d* 20/4) of from 0.9 to 1.05, and containing not more than 25% of paraffin oil, together with 5 to 40 parts of paraffin wax having a melting point of 155° F. to about 170° F. and containing at least 55% straight chain hydrocarbons, the content of straight chain hydrocarbons in the paraffin wax being higher, the lower the melting point of the wax within said range, said composition being emulsifiable in an aqueous disbursing medium in the presence of from about 5 to 40%, based on the weight of the non-aqueous portion of the emulsion, of emulsifying agent.

6. A composition capable of being dispersed in water to form an emulsion therewith, consisting essentially of from about 5 to 40% of emulsifying agent, from about 5 to 40% of a paraffin wax having a melting point of 155° F. to about 170° F. and containing at least 55% straight chain hydrocarbons, and from about 30 to 85% of an extract of petroleum predominantly made up of aromatics and naphthenic hydrocarbons and having a viscosity of at least 10 cs. at 210° F. up to solid compositions softening at about 200° F., an initial boiling point

of at least 300° F. at 1 mm. pressure of mercury, and a specific gravity (*d* 20/4) of from 0.9 to 1.05, and containing not more than 25% of paraffn oil.

7. A composition capable of being dispersed in water to form a stable emulsion therewith consisting essentially of from about 60 to 95% naphthenate bottoms of viscous, semi-solid consistency, the non-naphthenate fraction of which has a specific gravity (*d* 20/4) of about 0.995, a mixed aniline point of about 58° C., a molecular weight of about 918 and contains about 1% each of sulfur and nitrogen and from about 5 to 40% of paraffin wax having a melting point of 155° F. to about 170° F. and containing at least 55% straight chain hydrocarbons.

8. A mixture consisting essentially of from about 30 to 85% of a cyclic extract from the extraction of a lubricating oil fraction of petroleum with a polar solvent having a preferential solubility for aromatic hydrocarbons in the presence of paraffinic hydrocarbons, said extract having a viscosity varying from about 10 cs. at 210° F. up to solid compositions softening at about 200° F., an initial boiling point of at least 300° F. at 1 mm. pressure of mercury, and a specific gravity (*d* 20/4) of from 0.9 to 1.05 and containing not more than 25% of paraffin oil, together with from about 5 to 40% of emulsifying agent and from about 5 to 40% of a paraffin wax having a melting point of 155° F. to about 170° F. and containing at least 55% straight chain hydrocarbons.

9. Cellulose sized with a precipitate from an emulsion consisting essentially of water and naphthenate bottoms containing sodium naphthenates and cyclic petroleum components in the proportions of 5 to 40 parts of sodium naphthenate to 30 to 85 parts of cyclic petroleum components, said cyclic petroleum components having a viscosity varying from about 10 cs. at 210° F. up to solid compositions softening at about 200° F., an initial boiling point of at least 300° F. at 1 mm. pressure of mercury, and a specific gravity (*d* 20/4) of from 0.9 to 1.05 and containing not more than 25% of paraffin oil, together with from about 5% to 40%, in terms of the weight of the non-aqueous portion of the emulsion, of paraffin wax having a melting point of 155° F. to about 170° F. and containing at least 55% straight chain hydrocarbons.

10. Cellulose fibers sized with a precipitate from an emulsion in water of a mixture consisting essentially of 5 to 40 parts of sodium naphthenate emulsifier, 30 to 85 parts cyclic petroleum components which have a viscosity varying from about 10 cs. at 210° F. up to solid compositions softening at about 200° F., an initial boiling point of at least 300° F. at 1 mm. pressure of mercury, and a specific gravity (*d* 20/4) of from 0.9 to 1.05 and containing not more than 25% of paraffin oil, together with from about 5% to 40%, in terms of the weight of the non-aqueous portion of the emulsion, of paraffin wax having a melting point of 155° F. to about 170° F. and containing at least 55% straight chain hydrocarbons.

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