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METHOD OF SIZING PAPER

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12 Claims. (Cl. 92—3)

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This invention relates to the sizing of fibrous materials such as paper, cardboard, textile threads or fabrics, imitation leather, and the like. It deals with a new method of carrying out such sizing operations in a more advantageous manner and with novel compositions of matter which are not only valuable sizing agents but also have other useful applications.

The usual procedure in sizing fibrous materials is to contact intimately an aqueous dispersion of the size with the fibers and then precipitate the size on the fibers by adding a suitable precipitant. Thus, for example, in sizing paper pulp, the dispersion of size is generally added to the pulp in the beater or Holland machine and is there precipitated on the fibers with paper maker's alum or other acid-acting agents. In this method of sizing it is advantageous to use a sizing agent which can be prepared as a highly concentrated, stable aqueous dispersion or emulsion of small volume suitable for shipment and storage prior to use and capable of ready dilution to the relatively low concentration preferred in sizing without separation difficulties. A number of sizing agents, such as rosin, for instance, meet these requirements very well but are relatively expensive to use. Another suitable type of sizing agent is the emulsions of cyclic extracts of petroleum prepared with naphthenates of naphthenic acids having acid numbers of less than 200, which are described and claimed in copending application of Theodore F. Bradley, Serial No. 33,218, filed June 15, 1948. These sizing agents are not only relatively cheap but also are highly effective water-repelling agents. However, especially when using hydrocarbons of high viscosity, it is necessary in order to obtain uniform emulsions of small particle size to use extended agitation or other special emulsification procedures which add to the cost of operation and are undesirable. This type of difficulty is also encountered with other types of sizing agents such as many viscous resins, both natural and synthetic, waxes of high melting point, bituminous materials, asphalts, tars, etc., and has, in many cases, made their use impractical in spite of their desirable sizing properties.

An important object of the present invention is to overcome the foregoing disadvantages of these sizing agents and to provide sizing compositions which may be readily emulsified and will form stable emulsions of relatively small, uniform particle size capable of imparting good water-resistance to fibers of all types. Another object is to provide a convenient and efficient method of sizing fibrous materials which may be successfully used with viscous or solid sizing agents of the hydrocarbon type. A further object is to make available sized articles of manufacture, particularly sized paper or other cellulosic articles having desirable water-resistance. Still another object is to provide new emulsifiable compositions which not only are useful sizing agents but also have other important uses. Further objects and advantages of the invention will be apparent from the following description of some of its preferred applications, it being understood that the invention is not limited thereto but is broadly applicable in the scope set out in the appended claims.

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It has been found that fibrous materials, particularly fibers of cellulose and the like, may be advantageously sized with hydrocarbons in the presence of a polyphosphoric acid compound, preferably together with a mutual solvent for the polyphosphoric acid compound and the sizing agent used. Relatively small amounts of polyphosphoric acid compounds, preferably a salt or ester of a polyphosphoric acid, introduced into the sizing compositions containing viscous sizing agents, particularly hydrocarbons, markedly improve their properties making them easy to handle according to ordinary sizing procedures while giving excellent sizing characteristics. These new sizing compositions, comprising a viscous sizing agent together with a polyphosphoric acid compound, make it possible to supply the paper industry with a concentrated emulsible mixture which is readily dispersed in water and can be applied in the customary way in emulsion sizing. Emulsions produced from these compositions have the advantage of being capable of phase inversion. Thus, concentrated water-in-oil type emulsions can be prepared from sizing agents having viscosities of 400 SUS at 210° F. or higher viscosities without the use of a colloid mill or other costly dispersion methods due to the presence of the polyphosphoric acid compound. These water-in-oil type of emulsions are readily diluted to form stable oil-in-water type

emulsions of any desired concentration which are excellent sizing agents when applied in the usual manner. By preparing the new compositions either as emulsible mixtures of sizing agent and polyphosphoric acid compounds or as a water-in-oil or a concentrated oil-in-water type emulsion, the disadvantages of shipping and storing emulsions containing large percentages of water are avoided.

Among the polyphosphoric acid compounds which have been found to be suitable in the new sizing compositions of the invention, the derivatives of the polymetaphosphoric acids, $(HPO_3)_x$, and of the polyphosphoric acids of the pyrophosphoric acid type, $H_{x+2}P_xO_{3x+1}$, have been found to be especially advantageous. In these formulae of the preferred acids, x is at least 2, generally 2 to 6, although higher polyphosphates may also be used. Salts of these polyphosphoric acids are a particularly useful form of the phosphoric acid compounds used according to the invention. Such salts are readily prepared, for example, by fusing mixtures of orthophosphoric acid salts with bases or by fusing mixtures of salts of monophosphoric acids and polyphosphoric acids. In this way a large number of different polyphosphoric acid compounds can be produced, each differing only slightly from its adjacent members of the series and all being effective in the process of the invention.

When using polyphosphoric acid salts in the new sizing compositions, it is preferable as a rule to choose water-soluble salts, although by the use of suitable mutual solvents it is feasible to employ salts of very low solubility in water which might be classed as water-insoluble salts. Ammonium or alkali metal salts are particularly useful. Mixed salts as well as simple salts may be used, and with the polybasic polyphosphoric acids of high molecular weights, the mixed salts having both monovalent and polyvalent anions are particularly suitable. Thus, mixed salts having alkaline earth metal or aluminum or zinc ions together with alkali metal ions, for example, the calcium - sodium or magnesium - potassium or aluminum-ammonium salts of high polyphosphoric acids, can be used advantageously. With such salts it is preferred that the ratio of monovalent anions to polyvalent anions present be high, as the water solubility is thereby improved. Representative examples of other suitable polyphosphoric acid salts are, for instance, sodium trimetaphosphate $(NaPO_3)_3$, sodium tetrametaphosphate $(NaPO_3)_4$, sodium hexametaphosphate $(NaPO_3)_6$, tetrasodium pyrophosphate $Na_4P_2O_7$, disodium dihydrogen pyrophosphate $Na_2H_2P_2O_7$, trisodium hydrogen pyrophosphate $Na_3HP_2O_7$, sodium tetraphosphate $Na_6P_4O_{13}$, the complex fusion product from two moles of monosodium dihydrogen phosphate and one mole of disodium monohydrogen phosphate $Na_8P_6O_{19}$. As a rule the salts having a pH of 7 or higher are preferred and for this reason the salts of polyphosphoric acids of the pyrophosphoric acid type $H_{x+2}P_xO_{3x+1}$ are preferred over the polymetaphosphoric acid salts. However, by the use of buffers or the like any of the polyphosphoric acid salts may be successfully used. Buffers suitable for maintaining the desired alkalinity during sizing are, for example, sodium silicate, sodium borate, the orthophosphates such as disodium orthophosphate, etc.

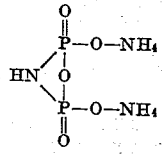
Thiopolyphosphates may be used in place of or in conjunction with the foregoing salts. Examples of salts of this type which are useful are, for instance, sodium monothiotetraphosphate $Na_6P_4O_{12}S$ and sodium trithiotetraphosphate $Na_6P_4O_{10}S_3$. These compounds have the same general efficiency as the other water-soluble polyphosphoric acid compounds in improving sizing according to the invention.

Another type of polyphosphoric acid compound which is effective in the compositions and process of the invention is the esters of these acids. Esters of aromatic hydroxy compounds, especially esters of polyhydroxy aromatic compounds such as pyrogallol, resorcinol, phlorogiucinol, hydroxyquinol, catechol, gallic acid, protocatechuric acid, digallic acid, ellagic acid, tannic acid, the tannins, tannin-like bodies, etc., are especially useful. Other suitable esters are, for instance, the esters of water-soluble mono- and polyhydric alcohols such as ethyl, isopropyl and tertiary butyl alcohols, glycerol, glycol, pentaerythritol, arabitol, polyvinyl and polyallyl alcohols, and the like. The pyrophosphoric and tetraphosphoric acid esters are equally suitable. Amino-substituted esters are an especially advantageous subgroup of esters useful in the new process. Esters of this type from amino anthraquinones are applicable according to the present invention. Hydroxyalkylaminoanthraquinones, wherein the hydroxyalkyl radical or radicals are attached to the aromatic nucleus through an intervening amino group, are emphasized in the patent but amino esters having the amino groups or groups otherwise attached to the molecule may also be used. Thus, the amino group may be linked to an aromatic nucleus either directly or through an intervening ester radical or acyl residue or by other groups. Suitable amino-substituted aromatic compounds from which the phosphoric acid esters may be derived include, for example, amino-benzene, amino-toluene, amino-naphthalene, amino-anthracene, amino-substituted phenols such, for instance, as the amino-phenols, amino-cresols, amino - resorcinols, amino - naphthols, amino-pyrogallols, amino-benzyl alcohols, amino-cinnamyl alcohols, amino-anisoles, amino-acetephenones, amino - benzophenones, amino - quinones, amino-benzaldehydes, etc. When the starting amino compound contains a hydroxy group as in the alcohols or phenols, the esters may be readily prepared by reaction with pyro, tetra or other polyphosphoric acid or anhydride or halogenide to form the amino esters which are useful in the present invention. With non-hydroxy starting materials, or where further hydroxylation is desirable, a suitable hydroxyalkylamino aromatic compound may be prepared by reacting the aromatic amino compound with glycol mono- and di-chlorohydrins or the corresponding chlorohydrins of glycerol or other polyhydric alcohols. This procedure is commonly carried out by dissolving the aromatic amino compound in a suitable inert solvent, adding the alkyl chlorohydrin, and refluxing until the reaction is substantially complete. The mixture is then made strongly alkaline with sodium or potassium hydroxide and the amine layer removed. After drying thoroughly, it may then be reacted with the polyphosphoric acid, anhydride, or halogenide. Tetraphosphoric acid is the preferred polyphosphoric acid for the synthesis of these esters because it is readily available in anyhdrous form.

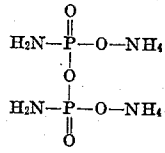
Addition products of methyl, ethyl, isopropyl, tertiary butyl and like esters of tyrosine, tryptophane, and creatine with the various polyphosphoric acids and their acid salts such, for instance, as mono-sodium dihydrogen pyro-

phosphate and the like, are equally useful in the new process.

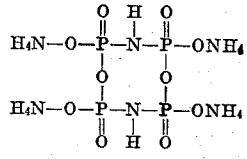
The polyphosphoric acid compound used may alternatively be an amino-polyphosphate of the type obtainable from ammonia and phosphorus pentoxide. Either the initial reaction products of the type



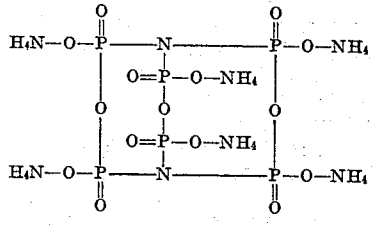
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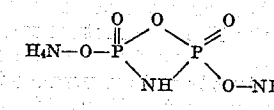
or the more complex products of further polymerization such as



or



i. e. ammonium hexaphosphate dinitride and products of higher molecular weight, may be used. Other water-soluble hexaphosphate dinitrides of any degree of polymerization such, for instance, as sodium hexaphosphate dinitrate or the corresponding potassium compound can likewise be employed. An alkali metal can replace either all the NH_4 groups of ammonium hexaphosphate dinitride or only a portion thereof. Thus, ammonium hexaphosphate dinitride can be treated with alkalies to a pH of approximately 8 without liberation of ammonia, but if caustic soda or soda ash is added beyond this point, the ammonium nitrogen is completely displaced and the pH will rise. The nuclear nitrogen, however, is not displaced by the addition of alkalies. Esters of these complex phosphates may be used instead of the salts. Thus, for example, the esters produced by reacting hydroxy organic compounds such as tannins, sugars, starches, cellulose, gums, lignins, aliphatic or aromatic alcohols, alkylolamine, etc. with molten ammonium imido diphosphoric acid



are suitable in the new process. These products are usually hard, brittle "glasses" which are soluble in water and probably involve condensation as well as esterification in their formation. Their structure has not been accurately determined but they have been found as a rule to be superior in the process of the invention to the imido diphosphoric acid salts, although these are themselves effective when used in suitable amounts.

As previously pointed out, the polyphosphoric acid compounds are preferably used with a solvent which is also substantially miscible with the sizing agent being used. Suitable mutual solvents are, for example, alcohols such as methyl, ethyl, normal propyl, isopropyl, normal or secondary butyl, the amyl alcohols, methyl isobutyl carbinol and the like, glycols such as the hexylene glycol, etc., hydroxy derivatives of polyhydric alcohols such as the mono- or poly-glycol monoalkyl esters or ethers having 1 to 4 carbon atoms in the alkyl group, ketones of the type of methyl ethyl ketone, mesityl oxide, diacetone alcohol, isophorone, methyl isobutyl ketone, etc., esters of which ethyl formate, methyl lactate and dimethyl maleate are examples, aldehydes as acetaldehyde and acetaldol or the like, diethylene dioxide, morpholine, phenols, and amines such as butyl or amyl amines, the ethanol amines, pyridines, etc. The particular solvent used should be one which boils at a temperature above that at which the sizing composition is prepared and/or used. Thus, when using sizing agents which are melted to facilitate their emulsification, it is preferable to employ higher boiling solvents; however, it is seldom that solvents boiling above about 150° C. are necessary.

The amount of polyphosphoric compound, or mixture of two or more such compounds, and solvent employed will depend to a certain extent upon the particular compound and solvent chosen and the sizing agent with which they are to be used, but as a general rule it has been found that about 0.25% to 10%, preferably 0.5% to 2.5%, of polyphosphoric compound based on the weight of sizing agent present is satisfactory. Less than 0.05% of polyphosphoric acid compound gives insufficient improvement of the sizing composition, while more than 20% may be detrimental to the effectiveness of the size. Sufficient solvent should be used to maintain the polyphosphoric compound homogeneously distributed in the composition, but too great an excess is to be avoided since it may reduce the water-resistance of the final sized product. Usually about one-half to ten times as much solvent by weight as polyphosphoric acid compound is suitable, two to about six times as much solvent being generally preferable.

Although other methods of incorporating the polyphosphoric acid compound in the sizing mixture may be successfully used, one procedure which has been found convenient comprises adding an aqueous solution of the chosen polyphosphoric acid compound to a mixture of the sizing agent and emulsifying agent which advantage-

ously may also contain the mutual solvent if such is to be used. Most preferably, the sizing agent is melted and thoroughly mixed with an acid emulsifying agent-forming compound such as naphthenic acids or rosin or an alkyl aryl sulfonic acid or the like, the mutual solvent is then added while continuing the mixing and heating, and then sufficient base to neutralize the emulsifying agent is run in together with the solution of the polyphosphoric acid compound. In this way emulsions of the water-in-oil type can be obtained which are stable, readily prepared without special expensive apparatus, and capable of phase inversion by dilution to produce oil-in-water type emulsions having excellent sizing properties.

The preferred sizing agents for use in the process and new compositions of the invention are hydrocarbons of higher molecular weight, most preferably the cyclic extracts of predominantly aromatic and naphthenic nature, obtainable by extracting petroleum or related oils, including hydrogenation products of coal and the like, with solvents which are selective for non-paraffinic constituents. A wide variety of polar solvents may be used for the preparation of such extracts, liquid sulfur dioxide, phenol, cresylic acid, furfural, beta,beta-dichlorethyl ether, nitrobenzene, the sulfolanes and sulfolenes, and the like being typical examples of suitable solvents. Combinations of solvents, as phenols with cresylic acid or liquid sulfur dioxide with benzene or toluene, for instance, are useful and the use of the so-called double solvent process employing mutually immiscible solvents, e. g. cresylic acid with propane, also gives suitable extracts. There are also advantages in reextracting the initial extract with an immiscible solvent to improve the selectivity of the extraction. Thus, extraction of Edeleanu extracts of lubricating oils with gasoline or the like has been found to improve the sizing properties of the compositions produced therefrom in accordance with the invention. Extractive distillation may be used in place of or in combination with the previously mentioned extraction methods.

Extracts of heavier petroleum oils such as the lubricating oils and residual stocks are especially useful in the new sizing compositions of the invention, but other fractions of petroleum or related hydrocarbon products can also be used successfully as sources of the extracts. The extracts may be derived, for example, from lubricant distillates or bright oils or cylinder stocks which may, for instance, range in gravity from 15° to 8° API at 60° F. They may be obtained from any mixed type petroleum oil such as Mid-Continent or Coastal or California crude or, in lower yields, from Pennsylvania type oils. For use in sizing in accordance with the invention, extracts boiling above 300° C. at 760 mm. Hg pressure are preferred, and most preferably extracts boiling from about 125° C. to 300° C. at 1 mm. Hg pressure are used. The more viscous extracts usually give the most desirable sizing properties and for this reason extracts having viscosities of at least 200 SUS at 210° F. are preferred. Most preferably, extracts having viscosities of 400 SUS at 210° F. or more are used and there are special advantages in using extracts having viscosities of the order of about 2,000 to 50,000 SUS at 210° F. Extracts obtained from narrow fractions, as described in U. S. Patent 2,115,960, may be advantageously employed. It is often advantageous to fractionate the initial extract to separate fractions of especially advantageous properties; thus, for instance, it has been found that the higher boiling 50% to 75% of an Edeleanu extract of lubricating oil gives superior sizing judging by permeability to water of sized paper. Other types of sizing agents which may be used include oils or waxes. These are useful when used either in combination or separately. Hydrocarbons such as lubricating oils, spindle oil, etc. may likewise be used. Various rubbers and synthetic resins such as are described, for example, in the article by E. G. Partridge entitled "Latex compounds for paper industry" in "India Rubber World," volume 118, pages 221 to 223 (May 1948), may be used as the sizing agent with phosphorus-containing compounds according to the present invention.

A wide variety of different emulsifying agents may be used in preparing the new emulsifiable compositions of the invention. Especially advantageous emulsifying agents are salts of naphthenic acids having acid numbers less than 200, preferably acid numbers of about 100 to 175, the acid number being the number of milligrams of potassium hydroxide which will neutralize the acids in a one-gram sample of the naphthenic acids. A suitable source of such naphthenic acids is the naphthenates produced in the refining of petroleum and its various products, particularly lubricating oil. The naphthenic acids having the preferred low acid number may be separated from their mixtures with less desirable naphthenic acids of higher acid number by fractionally distilling off the latter and using only those naphthenic acids boiling above about 200° C. at 0.5 mm. Hg pressure. Particularly suitable are naphthenic acids boiling between about 250° C. and 350° C. at 0.5 mm. Hg pressure. Petroleum oils which boil above 200° C. at 0.5 mm. Hg pressure, especially fractions of lubricating oil or the like boiling between about 250° C. and 350° C. at 0.5 mm. Hg pressure, are preferred sources of the naphthenates used in the new compositions. However, other emulsifying agents, including the ordinary commercial naphthenates having acid numbers greater than 200, fatty acid soaps, higher alkyl sulfate salts, organic sulfonic acid salts, particularly alkyl aryl sulfonates having 8 to 18 carbon atoms in the alkyl group, rosin acid soaps and the like or mixtures of any of these may also be successfully used. The amount of emulsifying agent which it will be most advantageous to use will vary somewhat with the type of emulsifier chosen and the particular sizing agent being emulsified but, as a rule, will correspond to about 3 to about 75, more preferably 5 to 50, per cent by weight of the total weight of emulsifying agent and hydrocarbon employed.

In preparing the emulsions by the neutralization technique previously referred to, a number of different types of basic compounds can be used. Hydroxides or carbonates of alkali metals or ammonia are suitable, sodium or potassium hydroxides being preferred hydroxides, however, because of their relatively low cost. The corresponding, particularly the sodium and potassium, carbonates require higher temperatures and are thus somewhat less preferable. Alkaline earth hydroxides such, for example, as calcium and magnesium hydroxides, etc. may also be used. For certain purposes, neutralization with an organic base such, for example, as aliphatic, alicyclic, or aromatic, primary, secondary or tertiary amines or quaternary ammonium bases, is advantageous. Water-soluble amines such, for

instance, as dimethylamine, propylamine, cyclohexylamine, the ethanolamines, etc. may be used in such cases. The chosen base is preferably employed as an aqueous solution of about 5% to about 30% concentration, most preferably about 5% to 15% concentration. The most stable emulsions are prepared by the use of slightly less than the stoichiometric amount of base, preferably about 85% to 95% of the amount required for neutralization of the acid of the emulsifying agent. A pH of about 8 to 13, preferably 10 to 11.5, is advantageous in the final emulsion. If the initial emulsion is too acid or alkaline, it can be brought to the desired pH by adding a suitable buffering agent.

The invention is, of course, not limited to the method of preparing the new emulsions described as other procedures are also applicable. Thus, for example, it is feasible to produce highly effective sizes by intimately mixing a sizing agent such as a cyclic extract of lubricating oil, for instance, with an emulsifying agent such as previously neutralized naphthenic or rosin acids and then adding a polyphosphoric acid compound either as an aqueous solution or a solution in the chosen solvent, followed by dilution with the required amount of water if insufficient has been added with the polyphosphoric acid compounds. Other possible variations in the emulsification procedure will be obvious, it being generally advantageous, however, to have the polyphosphoric acid compound and sizing agent in intimate contact and uniformly dispersed prior to application of the composition to the material to be sized.

It is a special advantage of the sizing compositions of the invention comprising a polyphosphoric acid compound, a sizing agent, preferably of relatively high viscosity, and an emulsifier that they not only are very effective in improving the water-resistance of fibrous materials but also are capable of ready emulsification and form stable emulsions of the water-in-oil type with hydrocarbon-type sizing agents, particularly the cyclic extracts of petroleum which may be readily inverted to emulsions of the oil-in-water type which are quite stable, yet are precipitable in the presence of paper fibers by the usual paper maker's precipitants. This unusual combination of desirable properties makes it feasible to prepare very cheaply highly effective sizing compositions as concentrated water-in-oil type emulsions which can be conveniently shipped at low cost, stored until needed, and readily diluted at the paper mill without difficulties from phase separation or loss in sizing power to form emulsions of the oil-in-water type which can be used for sizing in the same way as the conventional rosin emulsion sizes. Emulsions which contain at least 40% water, for example, 40% to 99% water or, as shown in Example I which follows, more than 99% water, can be thus used for sizing. Thus, in sizing paper, for example, the emulsions of the invention may be added to the pulp in the beater engine at any stage of beating, although as a rule it is more advantageously introduced when the beating has been substantially completed. The sizing may also be carried out in the Jordan machine or at the screens. A wide range of precipitants may be used for fixing the new sizing compositions on the fibers. Alum, aluminum sulfate, calcium chloride, acids such as sulfuric or hydrochloric acid, and the like are all suitable, but paper maker's alum is preferred. The precipitant may be added to the fiber along with the size but generally it is preferred to add it later in the process, thus providing adequate time for uniform distribution of the size before introducing the precipitant.

The amount of size which it will be most advantageous to employ will depend on the nature of the fibrous material being treated, the purpose for which it is intended, the type of sizing agent chosen, and the method of its application. As little as 0.2% based on the dry weight of the paper is effective but up to 20% or more may be used, the preferred range being usually about 0.5% to about 5%.

Most preferably a pH of about 4.5 to 6, depending on the type of pulp, is desirable during precipitation. If necessary, the pH may be controlled by adding dilute acid in the beater. About 25 grams of aluminum sulfate per kilogram of dry stuff in the beater gives satisfactory precipitation. Too much aluminum in the paper should be avoided as it adversely affects the permeability to water.

The following examples illustrate in greater detail some typical applications of the invention and show the advantageous results which may be obtained.

Example I

A series of sizing compositions was prepared using a variety of furfural extracts of different viscosities as the sizing agent and sodium pyrophosphate as the polyphosphoric acid compound. In each case, 800 grams of the extract were heated to about 80° C., 200 grams of wood rosin (FF) and 40 grams of isopropyl alcohol were charged in that order to a jacketed Readco Internal Mixer preheated to about 85° C. and mixed for 5 minutes. 106 grams of a 20% solution of sodium hydroxide and 100 grams of a 7.5% solution of sodium pyrophosphate were then added, and the mixing continued for 15 minutes at 80° C. to 85° C. The resulting water-in-oil type emulsion at 80° C. was poured into water sufficient, at the same temperature in a tall narrow vessel, to bring the concentration to 50% and stirred for 15 minutes at 80° C. with an Eppenbach Homomixer, care being taken to prevent incorporation of air into the oil-in-water emulsion. The stability and particle size of the emulsion were determined and the emulsion used to size test sheets of kraft paper prepared as follows:

A 1% slurry of kraft pulp was beaten 2 hours in the mixer and then diluted to 0.5%. One milliliter of the size emulsion diluted to 1% concentration was added per 100 grams of the dilute slurry and the stock stirred slowly for 15 minutes. Three-tenths of a milliliter of a 5% solution of aluminum sulfate was added and the stirring continued an additional 15 minutes. The sized pulp was formed into wet sheets in a sheet-making machine, pressed, and dried at 70° C. The sheets were conditioned for at least 2 hours at 75° F. and 50% relative humidity before testing for water-resistance by the dry indicator test and the fluorescence size test. In the dry indicator tests a mixture of 1 part fuchsin dye, 50 parts sugar and 1 part starch ground and sieved through a 100-mesh screen was brushed onto approximately 2 sq. ins. of the paper and the specimen floated in water maintained at 75° F. The time in seconds for the first visible change in color in the indicator due to wetting was recorded. The fluorescent size tests were carried out as described by van den Akket et al. in the "Paper Trade Journal," vol. 109, page 33 (1939). The following results were obtained:

Sizing agent	Viscosity S. U. S. at 210° F. of sizing agent	Fluidity of water-in-oil emulsion at 80° C.	Oil-in-water emulsion		Particle size microns	Sizing efficiency of paper corrected to sheet thickness of 10 mils	
			Stability at 50% concentration	Stability upon dilution to 1%		Dry indicator test (secs.)	Fluorescence size test (secs.)
Furfural extract of motor oil of 60 S. U. S. viscosity at 210° F.	79.8	Very fluid	Oil film on surface.	Some large particles coalesced.	A few >15; remainder 15 to 2; majority ca. 5.	32	54
Furfural extract of motor oil of 100 S. U. S. viscosity at 210° F.	208	do	Creamed but no coalescence.	Large particles settled but no coalescence.	A few >10; remainder 10 to 1; majority ca. 3.	26	63
Furfural extract of lubricating oil of 100 S. U. S. viscosity at 210° F.	392	do	do	Some large particles settled but no coalescence.	do	47	261
Furfural extract of motor oil of 150 S. U. S. viscosity at 210° F.	416	Very fluid gel.	do	do	do	35	298
Furfural extract of lubricating oil 200 S. U. S. viscosity at 210° F.	2,030	Fluid gel	do	do	A few >10; remainder 10 to <1; majority ca. 2.	41	195
Edeleanu extract of a topped Mid-Continent crude.	4,500	do	do	Large particles settled.	Some >20; remainder 20 to 1; majority ca. 3.	47	194
Edeleanu extract of a Mid-Continent crude residue.	25,600	Fluid gel which pours slowly.	Partial separation after 24 hrs.	do	Many >20; remainder 20 to 2; majority ca. 4.	44	300

Similar good results are obtained when sulfite pulp is used with these sizes instead of the kraft pulp.

Using 0.75% sodium hexametaphosphate based upon the total weight of aromatic extract and naphthenic acid in the size instead of the sodium pyrophosphate gives equally good results.

Example II

Using the method of Example I, sizing emulsions of the following composition were prepared using different emulsifying agents with an Edeleanu extract of a topped Mid-Continent crude as the sizing agent:

	Parts by weight
Extract	80.0
Emulsifying agent	20.0
Sodium hydroxide	1.9
Isopropyl alcohol	4.0
Sodium pyrophosphate	0.75
Water	100.00

The sizes were used to size kraft paper as in Example I and the papers were tested with the following results:

Emulsifying agent	Sizing efficiency	
	Dry indicator test	Fluorescence test
Naphthenic acids (acid number 150)	40	170
Rosin	47	194

Good results are also obtained when using a heavy asphalt (penetration 150) instead of the aromatic extract in the size. Other emulsifying agents such as petroleum sulfonates can be substituted for the naphthenic acids and rosin without detriment to the sizing efficiency.

Example III

To show the effect of the mutual solvent for the polyphosphoric acid compound, comparative tests were made with sizes prepared as in Example I using methyl ethyl ketone in place of isopropyl alcohol and omitting the solvent. In all cases the sizing agent was an Edeleanu extract of Mid-Continent petroleum having a viscosity of 4500 SUS at 210° F. and the test sheets were prepared and tested as described in Example I.

Parts of $Na_4P_2O_7$	0.75	0.75	0.75	0.75.
Solvent	None	Isopropyl alcohol.	Methyl ethyl ketone.	Methyl ethyl ketone.
Parts by weight of solvent.	None	4.0	4.0	2.5.
Fluidity of the water-in-oil emulsion at 80° C.	Gel	Fluid	Fluid gel	Fluid gel.
Percent size in paper.	1.9	1.9	2.0	1.9.
Sizing efficiency:				
Dry indicator test (secs.).	40	31	34	48.
Fluorescence size test (secs.).	255	200	293	394.

Amyl alcohol and methyl isobutyl ketone used in the same way as mutual solvents also give good results.

Example IV

A viscous Mid-Continent crude was emulsified with one-fifth its weight of naphthenic acids of acid number 150 using 0.75% by weight of sodium pyrophosphate and 2.5% of methyl ethyl ketone. The oil-in-water emulsion of 50% concentration was stable, although there was some creaming but stirring restored the emulsion to homogeneity. On dilution to 1%, the emulsion was very stable with the majority of particles less than 1 micron in diameter. Test sheets prepared with this emulsion as in Example I gave the following results:

Dry indicator test, secs. 48
Fluorescence size test, secs. 268

In the absence of a polyphosphoric acid compound, the emulsions were too unstable and in-

complete to warrant size testing with this viscous sizing agent.

Example V

In the same way a series of sizing emulsions was prepared from a viscous aromatic extract of a Mid-Continent crude using 20% of naphthenic acids of acid number 150 as the emulsifying agent and 0.375% to 1.5% of sodium pyrophosphate, together with 2% to 8% of isopropyl alcohol, as the solvent. In all cases good emulsion sizes of reduced viscosity compared with the corresponding emulsions without a polyphosphoric compound were obtained.

We claim as our invention:

1. A process of sizing paper pulp which comprises contacting an aqueous slurry of the pulp with an aqueous emulsion of a hydrocarbon having a viscosity of 400 to 50,000 SUS at 210° F. containing 0.05% to 5% by weight of said hydrocarbon of a polyphosphoric acid compound together with mutual solvent for said polyphosphoric acid compound and hydrocarbon, and adding an acidic agent to precipitate said emulsion on the pulp.

2. A process of sizing fibrous materials which comprises precipitating on the fibers particles from an aqueous emulsion of a viscous hydrocarbon effective as a sizing agent produced by heating said hydrocarbon and naphthenic acids to form a fluid mixture thereof having a lower viscosity, intimately contacting said mixture with an aqueous solution of 0.05% to 5%, based on the weight of hydrocarbon sizing agent, of a polyphosphoric acid compound and sufficient of a base to substantially neutralize the naphthenic acids, and diluting the resulting product with water to form an emulsion of the oil-in-water type.

3. A process of sizing cellulose fibers which comprises precipitating on the fibers particles from an emulsion of the oil-in-water type comprising 40% to 99% water, a liquid aromatic extract of petroleum hydrocarbons having a viscosity of at least 400 SUS at 210° F., an emulsifying agent in an amount of about 3% to about 75% of the total weight of emulsifying agent and hydrocarbon employed, and 0.05% to 5% by weight of said extract of a polyphosphoric acid compound.

4. A process of sizing paper pulp which comprises precipitating on the pulp particles from an emulsion 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 paraffins, 3% to 50% by weight of said extract of a water-soluble naphthenate, 0.25% to 5% based on the weight of said extract of a water-soluble alkali metal polyphosphoric acid salt, and at least 40 parts of water.

5. A process of sizing cellulose fibers which comprises precipitating on the fibers particles from an aqueous emulsion of a hydrocarbon having a viscosity of at least 400 SUS at 210° F., sufficient sodium rosinate within the range of 5% to 50% of the total weight of sodium rosinate and hydrocarbon employed to emulsify said hydrocarbon, and 0.05% to 5% by weight of said hydrocarbon of a water-soluble pyrophosphate, said emulsion being of the oil-in-water type and containing at least 40% of water.

6. A process of sizing cellulose fibers which comprises precipitating on the fibers particles from an aqueous emulsion of a sizing agent having a viscosity of at least 400 SUS at 210° F. and 0.05% to 5%, based on the weight of said sizing agent, of a polyphosphoric acid compound, said emulsion being of the oil-in-water type and containing at least 40% of water.

7. A process of sizing fibrous material which comprises precipitating on the fibers particles from an emulsion of a cyclic extract from the extraction of a lubricating oil fraction of petroleum with a solvent having a preferential solubility for aromatic hydrocarbons in the presence of paraffins, together with 3% to 50% of sodium salts of naphthenic acids having acid numbers less than 200, and 0.05% to 5% of a phosphate ester, said emulsion being of the oil-in-water type and containing at least 40% of water.

8. Fibrous material having on its surface a water-resistant coating precipitated from an aqueous emulsion comprising a sizing agent, an emulsifier therefor, and 0.05% to 5%, based on the weight of said sizing agent, of a polyphosphoric acid compound.

9. A paper product comprising cellulose fibers having distributed on their surface about 0.5% to 5% by weight of the dry fibers of a precipitate from the alum treatment of an aqueous emulsion of a hydrocarbon having a viscosity of at least 400 SUS at 210° F., an emulsifying agent, and 0.05% to 5%, based on the weight of said hydrocarbon, of a water-soluble polyphosphate.

10. In a process of sizing fibrous material by precipitating a sizing agent thereon, the improvement which comprises precipitating onto the fibers suspended particles from an emulsion of a hydrocarbon sizing agent having a viscosity of at least 400 SUS at 210° F. and naphthenic acids, which emulsion is formed by intimately contacting a fluid mixture of said hydrocarbon and naphthenic acids with an aqueous solution containing 0.05% to 5% by weight, based on the weight of sizing agent present, of a pyrophosphoric acid compound and sufficient of a base to substantially neutralize the naphthenic acids, and diluting the resulting product with water.

11. A process of sizing paper pulp which comprises precipitating on the pulp particles from an aqueous emulsion of petroleum hydrocarbons having a viscosity of at least 400 SUS at 210° F., 3% to 50% by weight of said hydrocarbons of sodium rosinate and 0.25% to 5% by weight of said hydrocarbons of sodium pyrophosphate, said emulsion being of the oil-in-water type and containing at least 40% of water.

12. A paper product comprising cellulose fibers having distributed on their surface about 0.5% to 5% by weight of the dry fibers of a precipitate from the alum treatment of an aqueous emulsion of a hydrocarbon having a viscosity of at least 400 SUS at 210° F., an emulsifying agent, and 0.05% to 20%, based on the weight of said hydrocarbon, of a water-soluble polyphosphate.

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