

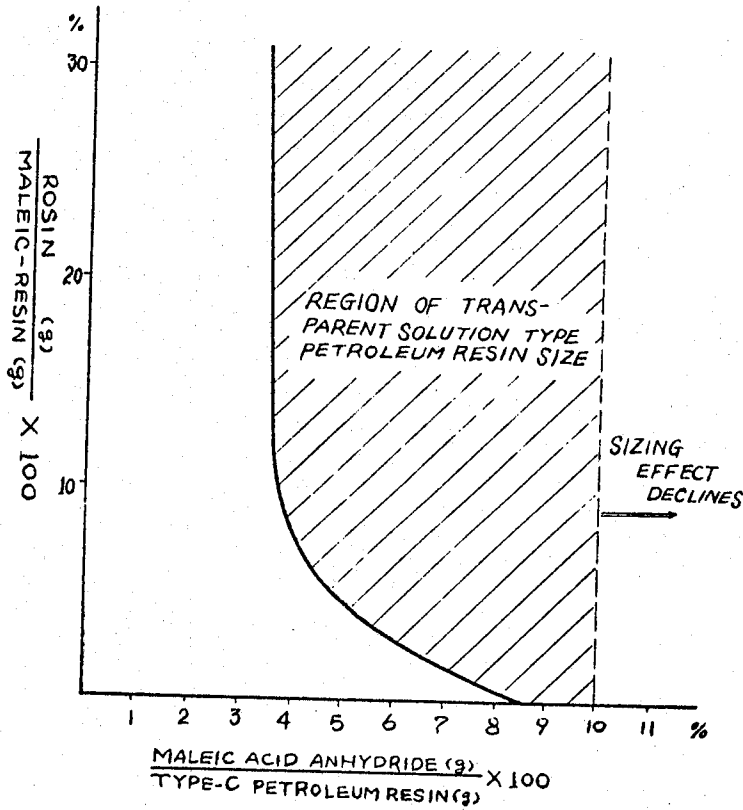
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METHOD OF SURFACE SIZING PAPER WITH A REACTION PRODUCT OF AN
UNSATURATED ACID AND A PETROLEUM RESIN

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METHOD OF SURFACE SIZING PAPER WITH A REACTION PRODUCT OF AN UNSATURATED ACID AND A PETROLEUM RESIN

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This is a continuation-in-part of U.S. application Serial No. 127,093, filed July 27, 1961, and is a full, clear and exact description.

This invention relates to a sizing composition for paper and more specifically to a sizing composition obtained from petroleum hydrocarbon resins, and is a continuation-in-part of our copending application Serial No. 127,093, filed July 27, 1961, now abandoned.

The petroleum hydrocarbon resins to which the present invention has application are thermoplastic, hard resins of light brown color having a bromine number of 10-70 and a softening point of 40-130° C. which may result from a copolymerization of highly unsaturated liquid fractions consisting chiefly of hydrocarbons of 5-10 carbon atoms produced in the refining or cracking of petroleum oil, said copolymerization reaction being conducted in the presence of Friedel-Crafts catalysts, and with the unreacted portion removed.

Prior art methods include attempts to adapt petroleum resins as a paper size. Most of these methods depend upon a process for treating a petroleum resin to form a colloidal dispersion with use of an emulsifier. Colloidal particles in such a dispersion often lack stability required for paper sizing, so that the particles tend to grow excessively large accompanying long shelf life. Moreover, these particles are originally so coarse that this type of size is found to be inferior to rosin size under the same service conditions. It is to be noted that the smaller the particle size the better the efficiency of a sizing composition.

Here, the inventors' finding about the structure in which rosin size firmly fixes to the paper fibers will be introduced. As is well known, the rosin sizing was first discovered by Illig and has long been used as highly important for paper manufacture. Since then, there have been made no appreciable improvements or discoveries qualified to replace his rosin size. The rosin size may be classified to a white emulsion type resulting from partial saponification of rosin and a brown transparent solution type resulting from a complete saponification of rosin. It is generally accepted that the white size is inferior in stability while the brown size is more reliable. The rosin size hereinafter referred to means the brown size.

The behaviour of an internal rosin sizing to fix in the paper fibers may be observed from a physical point of view as follows:

When rosin size is added to the pulp slurry, the rosin soap is hydrolyzed nearly completely to form fine colloidal particles of free rosin. These particles may be determined by electron microscope to be about a few hundred Angstroms in diameter. This diameter is small enough for the particles to pass in and out the interstices of the individual fibers which diameter is generally known to be about 1000 Angstroms. Since the fiber itself has a negative charge, the rosin size cannot become firmly bonded to the fiber due to an electrostatic repulsion. To permit stable attachment of the rosin size to the fiber system, alum or similar material with positive charge may be used to attenuate the negative charges on the two

substances sufficiently to overcome their electrostatic repulsion. The present inventors believe that rosin sizing agents are characterized by the action of such fine size particles to fix and stay in microstructure of the fiber so that the ultimate sizing effect is great.

Also employed with rosin size is a wax size produced by forming a non-polar substance such as paraffins into an aqueous emulsion with the aid of a suitable emulsifier. Although paraffins excell rosin in water repellency, the wax size is rather inferior in sizing effect as compared to rosin size when the former is used under the same conditions as the latter. Apparently, this is chiefly due to the fact that the colloidal particles of wax size are too large to rest in the interstices of a fiber. The same can be said of conventional petroleum resin sizes.

The colloidal particles in ordinary emulsions may be of several microns. Therefore, the petroleum resin sizes of an emulsion type are necessarily large in particle size, in fact much larger than rosin sizes, and hence cannot enter the interstices of the fiber. However, the reason that the conventional petroleum resin sizes are found to present a sizing effect to some extent in spite of their use in the form of an emulsion, may be accounted for by the fact that the addition of alum permits the size particles with resulting alumina flocks to rest in the macrostructure of the fiber. In other words, the function of such petroleum resin sizes to fix in the fiber system differs substantially from that of rosin sizes. Consequently, the firmness of bonding of the former sizing compositions to the paper fiber is quite unstable which would often invite serious trouble in the operation of paper making plants and would result in poorly finished paper products. This is the main reason why petroleum resin sizing agents prior to this invention have found very little use.

Whereas, it is the principal object of the invention to provide a petroleum resin sizing composition for paper which is qualified to replace the conventional rosin sizes.

It is another object of the invention to substitute petroleum resin for rosin in the manufacture of a sizing composition and hence to disclose a novel, useful application of such petroleum resin as is and will be more available in large quantities following the rapid progress of petrochemical industries.

It is a further object of the invention to provide sizing compositions of a solution type having an average particle diameter of less than 1000 Angstroms, having a high colloid stability and capable of dissolving transparently or semi-transparently in water, substantially different from known emulsion type petroleum resin sizes. By the average particle diameter is meant the diameter of a dispersion particle selected from the group of relatively large particles.

It is a still further object of the invention to provide novel means of applying such improved sizing compositions to paper whereby it is possible to manufacture a sized paper which is substantially water-proof and excellent in ink acceptancy and which has many advantages over conventional rosin size paper.

These and other objects and features of the invention will be more apparent from the following description.

As stated at the outset, the petroleum resins with which to prepare a sizing composition according to the invention result from the polymerization of highly unsaturated liquid hydrocarbon fractions which may be produced in the refining or cracking of petroleum oil. These hydrocarbon fractions may be subjected to copolymerization in the presence of a Friedel-Crafts catalyst thereby forming, upon removal of the unreacted portion, a relatively hard, light brown, transparent thermoplastic resin having a bromine number of 10-70 and a softening point of 40°-130° C. This resin may then be added and reacted

with maleic acid, fumaric acid, itaconic acid or other alpha-beta unsaturated polybasic acids or their anhydrides, followed by saponification with alkali thereby producing a sizing agent for paper.

The present invention is, however, more specifically concerned with a sizing composition which may be obtained with use of petroleum resins of such precise nature as defined below and which will exhibit an outstanding effect upon paper. The inventors have selected, from among highly unsaturated liquid hydrocarbon produced in the refining or cracking of petroleum oil, a fraction boiling at 20-100° C. and containing a diolefin of 5 carbon atoms and a fraction boiling at 140-280° C. and containing styrene or its derivatives, and have subjected the two fractions to copolymerization in the presence of a Friedel-Crafts catalyst. With the unreacted portion removed, the resulting petroleum resin was found to have a softening point ranging from 40° to 100° C. and a bromine number from 30 to 70. To this resin was added an alpha-beta unsaturated polybasic acid and alkali to saponify same thereby producing a solution-type petroleum resin size for paper.

The resin size thus obtained in accordance with the invention may be used equally for internal and external sizing procedures now in practice, regardless of the type of the starting resin compositions defined. The present invention should be construed concurrently as including improvements in and relating to the so-called external sizing method.

It will be appreciated that the petroleum resin per se is not inferior in water repellency to rosin and that such petroleum resin size comprising dispersion particles of only a few hundred Angstroms as above discussed can fully compete with rosin size. It will be also appreciated that the dispersion may change from the state of a suspension to the state of an emulsion, according as the diameter of the dispersion particles is reduced, and further to the state of a transparent solution. It is obvious that the dispersion with particle diameter of less than 1000 Angstroms will more closely approach the state of transparency. Such dispersion hereinafter referred to as a transparent solution type may be distinguished from an emulsion by microscopic examination; that is, the particles of the former are not resolvable by microscopic while those of the latter are easily resolvable. Here, it is the intention of this invention to provide a petroleum resin size of such transparent solution type.

The accompanying graph deals with petroleum resin size comprising a C-type resin which is later fully described. The graph serves to explain the relation of maleic acid anhydride added to the resin and rosin added to maleic-resin. The graph shows the amount of rosin in weight percent of maleic-resin (ordinate) as plotted against the amount of maleic acid anhydride in weight percent of petroleum resin type-C (abscissa).

It is already known that an alpha-beta unsaturated polybasic acid such as maleic acid anhydride can afford an alkali-soluble tendency to petroleum resin and this resulting resin is a satisfactory component coating material. However, petroleum resin reacted with such acid has never before been employed as a composition for paper sizing. It was discovered that when the addition compound is treated with alkali, the resin shows a high rate of dispersion and becomes an emulsion. Further studies revealed that the petroleum resin when reacted with maleic acid or its anhydride may be treated with alkali in a manner similar to rosin so that it may easily produce a soap solution and that this dispersion is highly useful as a sizing agent. However, it was further noticed that the soap solution exhibits a sizing effect which is inferior to rosin size when applied in the conditions under which the latter is normally employed. Furthermore, it was discovered that the efficiency of the petroleum resin size tends to deteriorate as the amount of addition of maleic acid anhydride is further increased,

resulting in increased resin saponifying tendency. It is believed that the phenomenon is due to an excessive increase in the hydrophilic nature of the reacted petroleum resin. On the other hand, it is necessary to use a sufficient quantity of maleic acid anhydride because without such a quantity it is difficult to obtain a stable dispersion through alkali treatment alone. It was determined by the inventors that the addition of maleic acid anhydride to the petroleum resin serves to maintain the minimum possible diameter of the dispersion particles and to keep the hydrophilic nature of the petroleum dispersion from increasing to an excessive extent, provided that said anhydride is added in certain determinate amounts. Maleic acid anhydride among other alpha-beta unsaturated polybasic acids when added in specific amounts, determines the quality of a resulting resin size.

To use of rosin, fatty acid, tall oil and other materials capable of turning into a water-soluble soap when saponified with alkali, or other emulsifiers such as nonionic surface-active agent and anionic surface-active agent is conducive to miniaturization of the dispersed particles in the reaction mixture of petroleum resin and maleic acid anhydride when treated with alkali. Such dispersion is a soap solution containing colloidal particles not resolvable by microscope and capable of presenting as effective sizing performance as rosin size when applied under ordinary commercial conditions. The saponifiable materials in this case are more or less assistant to emulsifier; therefore, adding such materials to the petroleum resin and thereafter treating this mixture with alkali cannot readily produce a stable dispersion.

The term alpha-beta unsaturated polybasic acid includes maleic acid, fumaric acid, itaconic acid and their anhydrides as well as citric acid capable of forming an alpha-beta unsaturated acid when heated. Citric acid, however, should be added in an amount twice that of the other acids mentioned.

The co-use of rosin or fatty acid provides an increase in the sizing effect and a pronounced effect when such material is heated, as this was proved by experiments conducted by the inventors. It is generally observed that maleic acid anhydride when added to petroleum resin remains partially unreacted. Commercial means to recover such unreacted portion of the anhydride economically is not simple. Furthermore, should the residual maleic acid anhydride exist in large quantities, it will sacrifice the intrinsic sizing effect of the resin size composition. It has been proven that addition of rosin, tall oil or unsaturated fatty acid to the maleic-resin helps remove the free maleic acid anhydride by virtue of its conjugate double bonds. At the same time, heat may be applied to the mixture to maintain same at reasonably high temperature for some time so that the unreacted maleic acid anhydride will undergo Diels-Alder reaction in which it readily combines with the added rosin, thereby removing substantially all of the free maleic acid anhydride that may be present in the reaction mixture. In this manner, the sizing effect may be greatly enhanced. The maleic acid anhydride adduct with rosin is known to act as a material fortification for the rosin sizing agent and have an excellent sizing effect for paper.

Most of presently available petroleum resins may be classed as type-B petroleum resin which is later described, and may be successfully used for coating. It is possible to produce a transparent solution type size eventually by adding maleic acid anhydride in amounts about 10% of the starting resin and further adding a sufficient quantity of rosin or the like. Increasing maleic acid anhydride increases the hydrophilic nature of the resin, but should the amount of this maleic acid anhydride increase far above the range of 10%, the sizing effect tends to decline sharply and such sizing agent can no longer be commercially acceptable. If large quantities of rosin were to be used to compensate for the adverse effect, it would not be compatible with the principles of the invention to sub-

stitute more easily available petroleum resins for expensive rosin.

There are many different types of petroleum resin which may be used for the preparation of a sizing composition for paper. Firstly, petroleum resin in the broadest sense as applicable for paper size is defined as type-A petroleum resin according to the invention. Secondly, the petroleum resin consisting in the main of C_9 liquid fraction selected from among highly unsaturated hydrocarbons produced in the refining or cracking of crude petroleum oil and having a relatively low bromine number, a relatively high molecular weight and a relatively high softening point is defined as type-B petroleum resin which has hitherto been used mostly for coating composition. Thirdly, the petroleum resin resulting from a copolymerization of C_5 fraction and C_9 fraction and having a relatively high bromine number, a relatively low molecular weight and a relatively low softening point is defined as type-C petroleum resin which is the latest, hence most desirable material for sizing.

The above three types of petroleum resin may be more clearly identified as follows:

	Type-A Resin (C_7 - C_{10})	Type-B Resin (C_9)	Type-C Resin C_5 and C_9 Copolymer
Bromine No.	10-70	10-30	30-70
Soft. point	40-130° C.	100-125° C.	40-100° C.
Mole. weight	500-1,600	900-1,600	500-900

When type-B resin and type-C resin are compared, the latter presents certain advantages over the former as will be apparent from the following.

The maleic-resin was found to disperse in water by alkali better the better the reactivity of resin with maleic acid anhydride. Based on this discovery, studies were made to improve the quality of type-B resin and, as a result, type-C resin was developed. While the type-B resin consists chiefly of C_9 fraction derived from the thermally cracked oil, the type-C resin results from the copolymerization of C_5 and C_9 fractions in the main which is so conducted that the resulting resin has a softening point ranging from 40 to 100° C. and a bromine number ranging from 30 to 70. The use of the type-C resin convinced the inventors of success in substituting a petroleum resin size prepared therefrom for conventional rosin sizes. The characters inherent in type-B and type-C resins will be discussed fully in examples given later. In preparing a sizing composition with use of the type-C resin, maleic acid anhydride may be added about 3.5-10% by weight of the resin. To this mass may be added a suitable amount of rosin, its derivatives such as maleic-rosin, tall oil or unsaturated fatty acid, whichever may be more readily available. The whole then may be saponified with alkali thereby producing a transparent solution type size. In such instance, if maleic acid anhydride is added more than 8%, the mixture may be turned into a similar sizing composition simply by alkali treatment. If, however, the amount of maleic acid anhydride is reduced below 8% it may be necessary to introduce a slight amount of rosin or its derivatives into the composition before it is saponified. The addition of rosin or its derivatives is intended to facilitate the production of the desired transparent solution on one hand and to enhance the sizing effect on the other. Difficulties were encountered when the amount of maleic acid anhydride added was less than 3.5% by weight of the resin, even with use of rosin. Reference to the accompanying graph shows the relation of maleic acid anhydride and rosin with respect to their respective mixing ratios. The slash-line area in the graph designates the composition of the resin capable of forming a transparent solution of sizing upon saponification. A dilute solution of this sizing composition presents under an electronic microscope a group of larger dispersion particles having an average diameter of the order of

a few hundred Angstroms, and these particles are uniformly distributed. From this fact, it is believed that the resin size of the invention is substantially identical with rosin size in the manner of bonding to the interstices of the fibers. It was confirmed by the inventors that the resin size of the invention compares rosin size in practical use at the paper manufacturing mill. One definite advantage of the sizing agent of the invention over rosin sizes of the prior art is that it produces very little foaming when applied to the pulp slurry. And, the petroleum resin size of the invention finds unparalleled application in the manufacture of extra-sized paper.

Similar with the application of rosin sizes, there may be employed alum or mixture of alum and sulfuric acid to cause the resin size to firmly fix in the microstructure of the paper fiber. For the same purpose, there may also be used cationic starch, polyethylene imine or the like which is usually applied as a cationic additive to the beaten pulp. It will be appreciated that the resin size of the invention may, when added with alum, be applied to the pulp slurry in very much the same way as rosin size is applied in the manufacture of sized paper.

As above stated, there may be used a variety of alpha-beta unsaturated polybasic acids, their anhydrides and citric acid in the preparation of petroleum resin sizing compositions according to the invention. However, a more preferred material would be maleic acid anhydride in terms of effectiveness and economy. In the same sense, rosin would be more advantageous for addition to maleic-resin than any other materials simply because rosin per se is a sizing material.

As already mentioned, there are two procedures adopted for applying the sizing. One is called an external sizing process or commonly termed as "tub sizing." The other is called an internal sizing process or commonly termed as "engine sizing" in the art. The product of the invention may be applied to both processes with equal results, but when applied to paper under special sizing conditions, the resin size of the invention permits the manufacture of extra-sized paper on accepted commercial basis.

Heretofore, paper was sized internally by rosin size in most cases. The yield at which resin in the rosin sizing composition fixes to the pulp fiber was about 60-70% of the total resin, while the remaining 30-40% was wasted in white liquor. The degree of sizing may be increased proportionally with an increase in the amount of the size to some extent, but would no longer advance beyond that extent of increase in the sizing agent, with all excess thereof being lost into the white liquor. Disadvantageously, uncontrolled increase in the amount of the size would often invite a serious situation such as what is commonly known as "pitch trouble."

The recent trend in demands for sized paper is directed to more intensely sized paper which can hardly be achieved by engine sizing. It is difficult to obtain such high sizing effect with warm water during hot seasons, no matter how much increase in the quantity of the sizing agent is attempted.

The significance of a sized paper is generally found in water repellency and in the elimination of ink blur over the paper. In this respect, a tub sized paper may be ideal because almost 100% of the resin can adhere to the paper to form a water-repellent film thereon, irrespective of the temperature of process water. Another advantage of the external or tub sizing procedure over the internal or engine sizing would be that loss of the sizing agent may be held at a minimum even when its quantity is increased considerably to intensify the sizing effect.

Most of modern paper making machines are equipped with a size press for performing the tub sizing work. This is another reason to believe that the tub sizing procedure is more easily practiced and economically handled as compared with the conventional rosin engine sizing methods.

As already mentioned, rosin per se is a water-repellent material. However, rosin soap which is the main component of a rosin size composition is a typical hydrophilic material. This rosin soap when fed to the pulp slurry turns into free colloidal particles of rosin by way of hydrolysis, and these particles with the aid of alum tend to adhere to the pulp fiber system. Therefore, rosin size cannot afford water-repellency to the surface of the paper if it is applied by tub sizing method.

Known tub sizing agents designed to give water-repellent tendency to paper are in general classed to wax size consisting primarily of paraffin and to fatty acid emulsion type size. These sizes have some water-repellent material dispersed in water using a suitable emulsifier. Such water-repellent material may compare with rosin insofar as water-repellency is concerned, but entirely differs therefrom in that it lacks adhesion inherent in rosin. Besides, the colloidal particles of a dispersion consisting of such water-repellent material are generally very coarse, and such dispersion lacks stability. Hence, paper sized with such tub sizing material is apt to deteriorate in quality, repel ink and become excessively slippery. Furthermore, the emulsifier in the size tends to deposit on paper and such unstable dispersion often causes operating failures at the paper making mill where paper is produced continuously in massive quantities.

In addition to the above sizing agents, a so-called reactive sizing composition such as alkyl ketene dimer is known but this size has hitherto found very little use on account of prohibitive price.

More recently introduced were a variety of petroleum resin sizes, none of which was satisfactory due to coarse resin particles. They were not capable of providing a requisite sizing effect on paper if they were simply coated on the paper. Any of these petroleum resin sizes of the prior art had the drawback that the colloidal particles in the dispersion were large and irregularly distributed, hence unstable to prohibit a long continuous operation of the paper plant.

Compared with conventional emulsion type resin sizes, the petroleum resin size of a solution type prepared according to the instant invention is more satisfactory in many respects. However, if it is applied by the usual method to paper, the solution type size cannot produce as satisfactory results as available with the new method of the invention. In other words, the water-soluble resin size has hydrophilic radicals attached partially to the molecules of the petroleum resin, said hydrophilic radicals causing the solution to penetrate the inner layer of the paper and marring the water-repellent properties of the resin. The tub sizing heretofore practiced would be satisfactory as the method of applying a size agent but has much to be desired before it is compatible with the specific type of a sizing composition used.

The method of applying a sizing agent to paper according to the invention comprises the step of adding alum to the pulp slurry in an amount of 1-5% (based on dry pulp weight) and the step of coating the paper with the solution type petroleum resin size of the invention. The method of the invention may be carried out with use of a size tub, size press or calender as well as on-machine and off-machine, and is intended to eliminate the difficulties encountered in the conventional rosin engine sizing and permit the manufacture of quality size paper at a minimum cost.

As will be understood from the above, the tub sizing procedure must meet the following requirements. The resin in the sizing composition should be comparable in water-repellency and adhesion with rosin and should be in the form of as fine colloidal particles as in rosin engine sizing when applied to paper so that a uniform, dense water-repellent film may be formed on the surface of the paper. These points were successfully covered by the unique method of the invention in which the pulp slurry

is initially treated with alum and is, after formed into paper, subjected to tub sizing.

The addition of alum to pulp leaves an acidic tendency and alumina in the resulting paper which act upon the resin size to decompose —COOM radical (M denotes alkali metal atom or ammonium radical) thereby eliminating its interference with water-repellency and rendering the paper resistant to penetrating solution of the size.

As already stated, the colloidal particle diameter of the resin size is less than a few hundred Angstroms and such fine particles can readily attach by the action of alumina with positive charge to the interstices of the pulp fiber.

Different from the usual internal or engine sizing, the sizing procedure of the invention takes place with the size stably resting in the microstructure of the paper fiber and forming a relatively thick, uniform water-repellent film on the surface of the paper. It is to be noted here that the use of rosin size in this instance of the invention yields no effect. This is because rosin soap decomposes in the presence of acidity on paper and tends to agglomerate thereby marring the finish of sized paper. The same may be said of the conventional emulsion type petroleum resin size because of its size particles being initially coarse.

Again, the sizing method of the invention is characterized by initially adding alum to pulp slurry before sheeted to paper and thereafter applying to the paper the solution type petroleum resin size of the invention, wherein the addition of alum is held in the range of 1-5%. This range of alum addition must be observed in order to assure the firm bonding of the size particles to the pulp fiber system. The amount of alum addition is somewhat greater than required for internal sizing. The reason for this is that alum addition in this instance of the invention is intended to concentrate the size particles at the surface portion of the paper to provide more effective sizing of the paper.

When the sizing method of the invention is compared with the conventional internal (engine) sizing method, both are seemingly identical for the latter usually applies the size and alum together to pulp slurry using a beater while the former applies alum and size separately. However, the results are different as will be apparent from the following.

Most of tub sizes intended to afford water-repellency to paper are of an emulsion type having a dispersed particle diameter of above 0.5 micron and therefore, tend to deposit in the gaps of the individual fibers and can hardly enter and fix in the microstructure of the fiber system. Whereas, the petroleum resin size of a solution type obtained according to the invention can be applied to paper by tub sizing with results comparable to sized paper prepared by internal sizing with rosin size. This is one of the features of the invention. Other features of the invention include freedom of influence by the temperature of feed water, and salt content therein, and elimination of differences in the finish of both sides of paper. Furthermore, it is made possible by the invention to eliminate the various troubles encountered in the paper making industry, which has experienced rosin sizing over a hundred and fifty years, including foaming in the pulp slurry, pitch deposit of the wire, smeared blankets and other difficulties either attributed to or aggravated by the sizing agents then used.

In practicing the invention, it will be apparent that there is required less size than in the conventional internal sizing and paper may be sized at a high rate of economy and efficiency by using the petroleum resin size of a solution type of the invention in lieu of expensive rosin size.

Further comparing the sizing method of the invention with the conventional tub sizing, it may be added that the use of alum as in the former is indispensable in view of its ability to accelerate the filtering of pulp slurry and enhance the yield of paper. Here is another advantage

of the invention in which pretreatment with alum of pulp slurry prior to sizing is concurrently effected in the first step of the sizing process.

In applying the solution type resin size of the invention to paper, there may be blended therewith other types of sizing agent, anti-forming agent or releasing agent as required so that a more refined sized paper may be obtained. It will be appreciated that the tub sizing according to the invention may also be applied to internally sized paper provided that such paper remains acidic and retains sufficient alumina to maintain the effect of the tub sizing agent of the invention.

The following examples are presented in further elucidation of some of the typical embodiments of the invention, and it is to be understood that these examples are illustrative of the principles of the invention and must not be taken in limitation of the scope and spirit of the invention.

The petroleum resins employed in all of the following examples have the physiochemical constants given below.

Color ----- C2 (Barlet method).
Softening Point ----- 80° C. (Ball and ring method).
Molecular Weight ----- 900 (Benzol freezing point method).
Bromine Number ----- 35 (ASTM method).

Example 1

I. Addition reaction of maleic acid anhydride with petroleum resin. The petroleum resin was melted and added with a predetermined amount of maleic acid anhydride and agitated at a temperature between 180° and 230° C. until reaction was completed. After the reaction, the resin was dissolved in ethyl-ether which was washed with water to remove unreacted maleic acid anhydride. The ethyl-ether layer was separated and the ether was removed by distillation to recover the resin. The resin thus recovered was checked for its saponification value. At the same time, water used to wash the ether solution was tested by titration with alkali to determine the amount of unreacted maleic acid anhydride. These results were listed in Table 1.

TABLE 1

Sample No.	A	B	C	D
1-1-----	3	3	4.1	22.4
1-2-----	5	3	5.6	38.5
1-3-----	10	3	13.3	71.4
1-4-----	15	3	17.0	94.7
1-5-----	20	3	20.6	129.5
1-6-----	10	1	29.5	57.1
1-7-----	10	5	5.2	77.9

Note:

A—Represents rate of maleic acid anhydride (percent)

$$= \frac{\text{Maleic acid anhydride (g.)}}{\text{Petroleum resin (g.)}} \times 100$$

B—Reaction time (hr.).

C—Rate of residue of unreacted maleic acid anhydride (percent)

$$= \frac{\text{Unreacted maleic acid anhydride (g.)}}{\text{Maleic acid anhydride initially added (g.)}} \times 100$$

D—Saponification value of reacted resin (after removal of unreacted maleic acid anhydride).

II-1. Saponification of maleic-resin by melting method. About 100 grams of the resin obtained in the process above (hereinafter referred to as the resin resulting immediately after the reaction, containing some unreacted free acids) was first heated to a molten condition, to which about 370 grams of dilute hot alkali solution was added gradually with agitation. The total amount of alkali was approximately 90% equivalents for total saponification value of the resin. As a result thereof, about 350 grams of petroleum resin dispersion was obtained, as the temperature was gradually lowered with vaporization of the alkali solution.

II-2. Saponification of maleic-resin by powdery method. About 100 grams of the resin obtained as in the foregoing was cooled to solidify the resin into a powdery form, which was then introduced gradually into a dilute boiling alkali solution of about 700 grams. In this manner, about 300 grams of petroleum resin dispersion was

TABLE 2

Sample No.	E	F	G	H
2-1-----	1-1	KOH-----	Molten-----	Nondispersible.
2-2-----	1-2	KOH-----	do-----	Partially coarse.
2-3-----	1-3	KOH-----	do-----	Milky emulsion.
2-4-----	1-4	KOH-----	do-----	Red-brown semi-transparent soap solution.
2-5-----	1-4	NaOH-----	do-----	Milky emulsion.
2-6-----	1-4	Triethanolamine-----	do-----	Red-brown semi-transparent soap solution.
2-7-----	1-6	KOH-----	do-----	Partially coarse.
2-8-----	1-7	KOH-----	do-----	Milky emulsion.
2-9-----	1-5	KOH-----	Powdery-----	Red-brown transparent soap solution.

Note:

E—Represents samples of reacted resins given in Table 1.

F—Alkali used.

G—Saponification procedures.

H—Dispersion.

obtained. The total alkali content was about 90% equivalents for the total resin saponification value. The resin dispersions thus obtained are illustrated in Table 2 above.

Example 2

The petroleum resin obtained in Example 1-I was blended with a predetermined amount of rosin and treated with a dilute hot alkali solution for saponification in a molten state to form a dispersion in accordance with the procedures of Example 1-II. Results obtained are listed in Table 3.

TABLE 3

Sample No.	I	J	K
3-1-----	1-1	10	Milky emulsion.
3-2-----	1-2	10	Red-brown semi-transparent soap solution.
3-3-----	1-6	30	Do.
3-4-----	1-2	5	Milky emulsion.
3-5 ¹ -----	(?)	10	Not capable of producing complete dispersion.

¹ At the above sample indicates a comparison test.

² Petroleum resin.

Note:

I—Represents samples of reacted resins given in Table 1

J—Rate of rosin added (percent)

$$= \frac{\text{Rosin (g.)}}{\text{Petroleum resin (g.)}} \times 100$$

K—Dispersion.

Example 3

The petroleum resin obtained in Example 1-I was added with rosin, and the reaction was continued at 180°–230° C. for about an hour. It was then treated with alkali according to the procedures of Example 1-II to produce a dispersion. The amount of unreacted maleic acid anhydride in the reacted resin was determined in accordance with Example 1-I. The results are listed below.

TABLE 4

Sample No.	L	M	N	O
4-1-----	1-1	10	Traces	Red-brown semi-transparent soap solution.
4-2-----	1-2	10	Traces	Red-brown transparent soap solution.
4-3-----	1-6	30	1.5	Do.
4-4-----	1-2	5	1.3	Milky emulsion.

Note:

L—Designates samples of reacted resins given in Table 1

M—Rate of rosin added (percent)

$$= \frac{\text{Rosin (g.)}}{\text{Petroleum resin (g.)}} \times 100$$
N—Rate of residue of unreacted maleic acid anhydride (percent)

$$= \frac{\text{Unreacted maleic acid anhydride (g.)}}{\text{Maleic acid anhydride initially added (g.)}} \times 100$$

O—Dispersion.

Example 4

In accordance with Example 1-II, Examples 2 and 3, maleic acid, fumaric acid, itaconic acid anhydride and citric acid were used in place of maleic acid anhydride, and fatty acid or tall oil was used in place of rosin in the process of forming a petroleum resin dispersion. For alkali treatment, only caustic potash was used and saponification was carried out while the resin was in molten state. The results are listed below.

TABLE 5

Sample No.	P			Q			R
	P'	P''	P'''	Q'	Q''	Q'''	
5-1-----	Maleic-----	15	3				Milky emulsion.
5-2-----	do-----	15	3	Rosin-----	30	Blended but not reacted-----	Red-brown semi-transparent soap solution.
5-3-----	do-----	15	3	do-----	30	1-----	Do.
5-4-----	Maleic anhyd-----	5	3	Oleic-----	10	Blended but not reacted-----	Do.
5-5-----	do-----	5	3	Tall-----	10	1-----	Do.
5-6-----	Fumaric-----	15	3	do-----	20	1-----	Do.
5-7-----	Itaconic anhyd-----	15	3	Rosin-----	30	1-----	Do.
5-8-----	Citric-----	20	3	do-----	30	2-----	Do.

Note:

P—Reaction of poly-basic acids

P'—Items

P''—Polybasic acid (g.)

$$\frac{\text{Petroleum resin (g.)}}{\text{Petroleum resin (g.)}} \times 100\%$$

P'''—Reaction time (hr.)

Q—Emulsification assistants

Q'—Items

Q''—Additive (g.)

$$\frac{\text{Petroleum resin (g.)}}{\text{Petroleum resin (g.)}} \times 100\%$$

Q'''—Reaction time (hr.)

R—Dispersion

From the data available of the above Examples 1 through 4, inclusive, the inventors have confirmed the following:

(1) *Addition reaction of maleic acid anhydride with petroleum resin.*—Maleic acid anhydride reacts with molten petroleum resin at optimum temperature of 150°–230° C. The reaction ends with maleic acid anhydride partially unreacted and remained in the reaction mixture. Experiments showed that maleic acid anhydride successfully reacted about 15% by weight of the petroleum resin.

(2) *Effect of alkali upon maleic acid anhydride in petroleum resin.*—When more than 10% of maleic acid anhydride was added to type-B petroleum resin and saponified with alkali, a transparent soap solution (milky emulsion) was obtained. The colloidal particles of this soap solution were so fine as irresolvable by microscopic examination and were highly stable. The reacted resin was found to be a mixture of petroleum resin and maleic acid anhydride added thereto. Alkali addition caused the maleic-resin mixture to exhibit strong emulsifying action. The alkali which may be used according to the invention includes caustic soda and caustic potash. The latter, however, was more effective. Alkali carbonate, triethanol amine and the like may also be used. The optimum amount of alkali was about 70 to 95% equivalents for total saponification value of the reacted resin containing some unreacted acids.

(3) *Effect of rosin addition upon maleic acid anhydride in petroleum resin.*—It was confirmed that addition of rosin to the petroleum resin, after maleic acid anhydride was added thereto, facilitated the formation of a good emulsion upon saponification. This consisted of very fine colloidal particles and was highly stable. In this instance, rosin soap acted as an emulsifier for petroleum resin, but such fine colloidal particle formation was attributed to the action of a very small amount of resin-maleic adduct soap. This indicates that rosin addition to the maleic-resin mixture accelerates the formation of a solution type petroleum resin size embodying this invention.

(4) *Effect of rosin reaction with resin-maleic adduct.*—As already stated, maleic acid anhydride when added to petroleum resin remains partially unreacted. It was found possible to combine these free maleic acid anhydride portions with rosin through Diels-Alder's reaction by maintaining the mixture at a reaction temperature after rosin was added. The temperature at which maleic acid anhydride reacted with rosin was substantially the same as that for reaction with petroleum resin.

(5) *Use of citric acid, fumaric acid, itaconic acid and their anhydrides in place of maleic acid anhydride, and use of fatty acid and tall oil in place of rosin.*—Maleic acid anhydride owes its reaction with petroleum resin to its unsaturated double bond. From this fact, it will be understood that organic polybasic acids having such unsaturated double bond including maleic acid, fumaric acid and itaconic acid anhydride may be equally employed. It was ascertained by experiments that these polybasic

acids, though somewhat inferior in reactivity to maleic acid anhydride, exhibited substantially similar results. In place of rosin, there may be employed fatty acid, tall oil or similar substances capable of forming a soap with alkali treatment, which yielded as effective results as rosin.

The following examples are presented in illustration of the sizing effect of each of the sizing compositions prepared in accordance with the invention.

Example 5

Handsheet studies were made to determine the sizing effect of each size composition.

1. *Preparation of handsheet.*—Sheet pulp (BKP (L) 50° SR) was beaten by Rubass beater and manually squeezed to about 70% of water. This was then stirred up and disposed overnight in a sealed chamber. BKP (L) 50° SR designate kraft plup made of a broad-leaf tree having a freeness of 50° by Shopper-Riegler method. This wet pulp of a predetermined amount was placed in a mixer and defiberized to about 4% pulp consistency with addition of water. Engine sizing was carried out by adding to the pulp a size equivalent in quantity to 1% of a resin constituent based on dry pulp and alum solution equivalent to 2% of hydrous crystals. The stock was placed on TAPPI standard handsheet machine. The handsheet paper of about 65% in water content was prepared. This was wind-dried and thereafter, put on a

dryer of 1.3 kg./cm.² steam pressure and thus dried for about 3 minutes. The sheet thus obtained weighed about 60 g./m.².

II. *Measuring the sizing effect.*—The dry handsheet was disposed for about 24 hours in a chamber having a humidity of 65% and a temperature of 20° C. and thereafter tested by Stöckigt method. The Stöckigt method is a testing procedure wherein a sample paper is floated in a 2% ammonium rhodanide solution, followed by placing a droplet of 1% ferrous dichloride solution on to the paper and the time taken for red spots to appear on the surface of the paper is checked by a stop watch, the time thus read being the velocity of water permeating the sample paper.

Table 6 shows the results of the test made on each sample sizing agent.

TABLE 6

Sample	S	T
6-1	2-3	12.2
6-2	2-4	9.5
6-3	2-5	9.4
6-4	2-6	9.8
6-5	2-8	13.8
6-6	2-9	3.0
6-7	3-1	28.5
6-8	3-2	29.0
6-9	3-3	30.0
6-10	3-4	28.4
6-11	4-1	31.4
6-12	4-2	31.0
6-13	4-3	30.6
6-14	4-4	30.3
6-15	5-1	4.1
6-16	5-2	22.0
6-17	5-3	24.0
6-18	5-4	27.0
6-19	5-5	29.0
6-20	5-6	20.0
6-21	5-7	22.0
6-22	5-8	25.0
6-23	(9)	30.5

¹ Comparison test.

² Brown rosin size.

NOTE: S—Designates sizing agents used in each example.

T—Stöckigt sizing value (sec.).

It was observed that when alum solution was added to the stock in the mixer, the sizing agent of the invention exhibited less foaming as compared to rosin size.

Experiments conducted by the present inventors show that better sizing is obtainable with the type-C petroleum resin of the instant invention than with the type-B petroleum resin which finds more use in the preparation of coatings. Data supporting this fact are presented in the following example.

Example 6

The petroleum resins used in this example for purposes of illustration are of the following properties.

	Type-B petroleum resin	Type-C petroleum resin
Main component	C ₉ fraction	C ₈ and C ₉ fractions=1:1.
Color (Gardner)	12	12
Softening point (Ball-and-Ring method)	110° C.	73° C.
Bromine number (ASTM)	19	53.
Molecular weight (Benzene Freezing Point method)	1013	803.

I. *Size preparation.*—Each of the above petroleum resins was placed in a round-bottom flask attached with an agitator, wherein the resin was heated to melt and thereafter added with a predetermined amount of maleic acid anhydride. The mixture was subjected to reaction under agitation at a temperature between 170° C. and 230° C. for about 3 hours and thereafter added with rosin, oleic acid or tall oil (or this addition may be omitted) followed by saponification with dilute caustic potash of 90% equivalent for the total saponification of the resin. The resulting dispersion was further diluted with water to 40% strength of the resin.

II. *Handsheet preparation.*—The handsheet was prepared in accordance with the procedures outlined in Example 5-1.

III. *Determination of sizing effect by handsheet.*—The two types of sizing composition obtained in this example were compared for sizing performance using handsheets to which the respective sizes were applied. This comparison test included rosin size for a better illustration as given in the following table.

TABLE 7

Sample No.	Resin	Organic Acid	Rate Percent U	Additive to Reacted Resin	Rate Percent V	Dispersion W	Handsheet Stöckigt test (Sec.)
1 X	B			Rosin	100	Extremely large particle, hence unusable.	
2	B	Maleic acid anhydride	15			#	10
3	B	Maleic acid	10			#	18
4	B	Fumaric acid	10			#	16
5	B	Itaconic acid anhydride	10			#	18
6	B	Citric acid	20			#	15
7	B	Maleic acid anhydride	10	Rosin	10	#	18
8	B	do	15	do	10	## (Slightly turbid)	12
9	B	do	10	Oleic acid	10	#	13
10	B	do	10	Tall oil	30	#	17
11 Y	B	do	10	Rosin	10	#	22
12 Y	B	do	10	Oleic acid	10	#	17
13	B	do	10	Rosin	100	## (Semitransparent)	26
14	C	do	5			#	18
15	C	do	8			## (Slightly turbid)	25
16	C	do	12			## (Transparent)	15
17	C	do	2	Rosin	10	#	20
18	C	do	5	do	10	## (Semitransparent)	31
19	C	do	8	do	10	## (Transparent)	26
20	C	do	12	do	10	do	15
21	C	Maleic acid	5	do	10	## (Slightly turbid)	31
22	C	Fumaric acid	5	do	10	do	30
23	C	Itaconic acid anhydride	5	do	10	do	30
24 Z	Rosin					do	27

NOTE for the above table:

U— $\frac{\text{Organic acid (g.)}}{\text{Petroleum resin (g.)}} \times 100$

V— $\frac{\text{Additive (g.)}}{\text{Reacted resin (g.)}} \times 100$

W—#: Emulsion type dispersion. ##: Transparent solution type dispersion.

X—Comparison test: Mixture of resin and rosin (1:1) emulsified with alkali solution.

Y—Maleic-resin was added with the above identified additive and continued for reaction at 170–230° C. for about 3 hours to combine free maleic acid anhydride with the additive.

Z—Rosin size.

15

Example 7

The manner in which the solution type petroleum resin size is applied to paper by tub sizing method is illustrated as follows, together with data showing its sizing effect.

I. Paper (handsheet) preparation.—Beaten wet pulp (BKP L.N. 1:1 mixed 30° SR) in a flask of 500 cc. and shaken. This was treated with the size and alum in the respective amounts specified in Table 8 thereby producing an ordinary engine-sized paper. The tub sizing as indicated in Table 8 was also applied in which alum was added to pulp slurry and the pulp was then shaken and placed on TAPPI standard machine to produce a handsheet of paper to which the size was applied.

II. Tub sizing.—Paper was immersed in a dilute tub sizing agent having 2.5% resin consistency and pressed between rolls. The amount of this dilute solution deposited on paper was about 100%. The sized paper then was dried by a steam dryer (2 kg./cm.² steam pressure) for about 3 minutes.

III. Determination of sizing value.—The sized paper was tested by Stöckigt method and also by ink floating method which is designed to measure the time taken for ink to blur on a test piece of paper after dropped thereon, the ink being an ordinary writing blue black ink.

5

10

15

20

16

Example 9

Alum was added in varied amounts to pulp slurry, and the resulting paper was subjected to tub sizing in accordance with the procedures of Example 5.

TABLE 10

Alum addition (percent)	Paper, pH	Size deposit (percent)	Sizing value (sec.)	
			Stöckigt	Ink float.
0.....	6.0	2.57	12.0	21
1.....	5.3	2.55	45.5	1,140
2.....	5.2	2.57	48.6	1,080
3.....	5.1	2.57	49.0	1,740
4.....	5.1	2.57	47.9	1,760
5.....	5.1	2.55	46.7	1,470

NOTE: Sizing value was maximum at 3% of alum addition. Further increase in alum gave no appreciable change in the pH of the paper but caused a slight decline in the sizing effect.

It will be appreciated that the above Example 9 together with data in Table 10 may be equally applied to Examples 7 and 8.

While certain specific forms of the invention have been described in some detail together with the theories which

TABLE 8

Sample No.	1	2	3	4	5	6	7
Engine Sizing with alum: Type of Size.....	Rosin size..	Solution type petroleum resin size.					Rosin size.
Quantity*, percent.....	2.5.....	2.5.....					1.0.
Alum**, percent.....	3.1.....	3.1.....			2.0.....	2.0.....	2.8.
Tub Sizing: Type of Size.....			Rosin size..	Solution type petroleum resin size.	Rosin size..	Solution type petroleum resin size.	#Solution type petroleum size.
Deposit***, percent.....			2.5.....	2.5.....	2.5.....	2.5.....	1.5.
Sizing Value: Stöckigt method (sec.).....	36.7.....	36.6.....	0.....	7.0.....	6.5.....	52.6.....	41.6.
Ink floating method (sec.).....	1,620.....	1,440.....	0.....	5.0.....	3.0.....	2,400.....	2,460.

NOTE:

*Based on resin content on paper.

**Based on solid content on paper.

***Based on resin content as calculated from the amount of dilute size solution deposit on paper.

#Dilute solution containing resin of 1.5% consistency.

Example 8

The sizing effect was determined of each of the following tub sizing agents applied to unbleached kraft paper made from needle-tree pulp stock and weighing 100 grams per square meter, with use of alum.

- (1) Solution-type petroleum resin size.
- (2) Alkylketene dimer emulsion.
- (3) Starch (soluble starch).
- (4) A blend of solution-type resin size and alkyl ketene dimer emulsion (mixed at the ratio of 1:1 based on solids).
- (5) A blend of solution-type resin size and starch (mixed at the ratio of 1:1 based on solids).

The results are given in Table 9 below.

TABLE 9

		Deposit (percent)	Stöckigt method (sec.)	Bursting strength, kg./cm. ²	Picking test Denyson wax No.
1.....	Solution-type petroleum resin size.....	2.0	115	4.8	8A
2.....	Alkylketene dimer emulsion.....	2.0	146	3.6	7A
3.....	Starch.....	2.0	0	5.1	14A
4.....	Blend of (1) and (2).....	2.0	163	4.1	8A
5.....	Blend of (1) and (3).....	4.0	119	5.1	11A

Now, the effect of alum addition is illustrated in Table 10. Alum gives maximum effect on sizing at 3% and shows no appreciable increase in its effect when added in excess of 3%. The inventors define the optimum range of alum addition to be from 1 to 5%. Should it exceed the upper limit, alum affects the freeness of paper and furthermore, it is not wise to use any excessive amount of alum from an economical point of view.

it is believed to best explain their functions, it is to be understood that the invention is not limited to the precise procedures described nor is it dependent upon the accuracy of the theories which have been advanced. On the contrary, the invention is not to be regarded as limited except insofar as possible limitations are included within the terms of the accepted claims in which it is the intention to claim all novelty inherent in the invention as broadly as is permissible in view of the prior art.

Having thus described the invention, what is claimed and desired secured by Letters Patent is:

1. A sizing method comprising adding alum to pulp slurry in an amount of 1 to 5% based on dry pulp weight

and making the pulp into a web of paper, and applying to the surface of the paper a saponified petroleum resin size of the character which is obtained from reacting a compound selected from the group consisting of alpha-beta unsaturated polybasic acids and their anhydrides in the presence of Friedel-Crafts catalyst, with a hard, thermoplastic resin resulting from a copolymerization of liquid hydrocarbons of 5-10 carbon atoms having a bromine

number of 10-70 and a softening point of 40°-130° C., said size being in the form of a dispersed solution of particles having an average particle diameter of less than 1,000 Angstroms and the addition of alum providing an acidic condition which develops the sizing property of the resin in the paper.

2. The method as claimed in claim 1 wherein said petroleum resin size is obtained from reacting at 150°-250° C. said compound with petroleum resin resulting from a copolymerization of a liquid hydrocarbon fraction containing diolefins of 5 carbon atoms and boiling at 20°-100° C. and a liquid hydrocarbon fraction containing an aromatic hydrocarbon selected from the group consisting of styrene and its derivatives and boiling at 140°-280° C., said polymerization being conducted in the presence of Friedel-Crafts catalyst, and said petroleum resin having a softening point of 40°-100° C. and a bromine number of 30-70, and the amount of said polybasic acid being 3.5-10% by weight of the total petroleum resin.

3. The method as claimed in claim 2 wherein said petroleum resin size is admixed with a saponifiable compound selected from the group consisting of rosin, tall oil and unsaturated fatty acids.

4. The method as claimed in claim 3 wherein said resin size is maintained in reaction with said saponifiable compound further at 150°-250° C. until the latter has combined with any unreacted alpha-beta unsaturated polybasic acid.

5. The method as claimed in claim 1 wherein said petroleum resin size is obtained from reacting at 150°-250° C. said compound with petroleum resin resulting from a copolymerization of a liquid hydrocarbon fraction containing diolefins of 5 carbon atoms and boiling at 20°-100° C. and a liquid hydrocarbon fraction containing an aromatic hydrocarbon selected from the group consisting of styrene and its derivatives and boiling at 140°-280° C., said polymerization being conducted in the presence of Friedel-Crafts catalyst, and said petroleum resin having a softening point of 40°-100° C. and a bromine number of 30-70, blending the reaction mixture with a saponifiable, lipophilic material, and thereafter subjecting the reaction mixture to saponification with alkali.

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