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3,392,085

METHOD OF SIZING PAPER WITH A FATTY ACID AND CARBOHYDRATE

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ABSTRACT OF THE DISCLOSURE

A method of making sized paper having improved resistance to alkaline environments wherein the paper pulp is treated with a mixture of a sodium, potassium, or ammonium salt of a substantially saturated fatty acid, and a cationically active starch or gum, or hydrogen bonding starch or gum.

This invention relates to the production of sized fiber articles which have high resistance to penetration by various liquids. More particularly, the invention relates to a method of sizing fibers which may be carried out over a wide pH range. The invention also relates to a fiber product size which is used in the method and to the fiber products produced therewith.

Sizes employed in the prior art have been used to produce fiber articles due to their imparting to such articles the ability to resist penetration by various liquids, as well as to increase the strength of the fiber articles. Resistance to water penetration is a first sizing property. By the term "resistance" a total lack of penetration is not intended, rather, a good holdout against such liquids is sufficient to enable relative measurement of such properties and an increased service life. In the normal uses of papers, they must resist such materials as inks, ambient moisture and often, various hot and cold liquids of both acid and/or alkaline pH's.

Another approach of long standing is to coat the relatively unsized paper with a paraffin material to provide water resistance. Such products have been employed for many years as butchers' wraps, soap wrappers and packaging wraps for slightly deliquescent materials. The coating of lightly sized papers with such water resistant materials is an expensive process.

For the the economic sizing of paper, it must be accomplished during the formation of the paper in conventional paper making equipment and with chemicals having low cost and, preferably, involving few purifying or previous synthesizing steps. A widely employed process of sizing paper which meets these economic requirements involves the setting or precipitating of rosin size on the fibers in an aqueous suspension with a precipitating agent of aluminum sulphate over the pH range of 4.5 to 6.0. In this acidic pH range, the cellulosic fibers are weakened somewhat, but due to the presence of the rosin size, the overall product has superior properties to those of unsized or blotter paper. When a rosin or fortified rosin size as used in many commonly employed paper making processes is attempted to be set or precipitated at pH's greater than about 6.5, the size does not precipitate within the body of the fibers and practically no sizing effect is obtained. Over the pH range which can be employed for the setting of rosin or fortified rosin sizings, 4.5 to 6.5 pH, there is practically no resistance to penetration by alkaline substances.

The need for fiber articles and papers having resistance to penetration by various chemical substances and including alkaline materials has been met generally in the art by the use of chemically synthesized sized material. A general drawback of such synthetic sizes is their great expense. Such expensive sizes have been referred to here-

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in as commercial alkaline resistant size. These may be employed in conventional paper making equipment but are not precipitable with alum.

It has been previously known that an economical sizing process could be carried out for imparting some general sizing properties including alkaline resistivity to cellulosic fiber products by mixing with the aqueous suspension of fibers the potassium or ammonium salts of low unsaturated content fatty acids and then precipitating their insoluble soap compounds by addition of a material releasing a polyvalent metallic ion, such as alum. The sodium salt of such fatty acids could not be employed for the commercial sizing of the paper due to the fact that it is insoluble at the temperatures at which it is necessary to operate conventional paper making equipment. Most paper machines or Fourdrinier machines have a water temperature of 90° F. to 135° F. As the sodium salt of such fatty acids in a 4% solution at elevated temperatures of approximately 150° F. begins to ball and clump at approximately 138° F. and is totally solidified at 130° F., it cannot be used as a true solution in conventional paper making equipment. An obvious suggestion for this difficulty with the use of sodium salts of fatty acids would be to increase the temperature of the paper making mill. At temperatures upward of 135° F., the rubber parts on Fourdrinier machines, cardboard cylinder machines, and hand-sheet paper machines are deleteriously affected. Another problem which was located when use of sodium salts of fatty acids was attempted was that the salts ball and clump in the lines when such are shut off or when the paper making equipment is shut down. The sodium salts solidify and plug the size lines and are extremely difficult to remove. In total, the use of the sodium salts of the fatty acids in the above manner, alone, is not practical. It is often necessary to run paper making equipment, particularly large Fourdrinier machines, at lower temperatures between 90–110° F. and at such temperature the above effect cannot be adequately alleviated.

Another general drawback to the use of the potassium and ammonium salts alone is that they can only be precipitated at rather low formation pH's, in the acidic range. Such a sizing process tends to weaken the cellulosic fibers as set out above.

Another prior sizing process which is known to the inventor is to size paper with an aqueous emulsion of low unsaturated content fatty acids which are held in an emulsion form by the presence of an emulsifying agent. Such fatty acids may then be precipitated within the body of the fibers with either the prior or subsequent addition of alum. In such a sizing process employing free fatty acids and the alum to form the water insoluble soaps of the fatty acids, it is necessary to carry out the precipitation reaction at a low pH, thus weakening the cellulosic structure of the fibers.

The prior alum precipitation sizing processes mentioned herein are all necessarily carried out over a rather narrow acidic pH range. While operating within such range is entirely economically feasible, it would be desirable for certain products and certain properties in the final products to operate over a wider pH range and to have that pH range extend to above 7.0 pH. None of the prior processes mentioned herein are operative in a manner to meet these criteria.

A brief description of the invention by which the above problems may be overcome is the following. Cellulose fibers are refined to a desired fiber length and then diluted with water to form a desired aqueous suspension consistency. The aqueous suspension is maintained at an elevated temperature and a homogeneous mixture of fatty acid salts and a water soluble cationic material is then added to the aqueous suspension either prior to or following the addition of a water soluble precipitating

Another object is to provide a method of internally sizing fiber articles which exhibit resistance to chemical substances, including alkaline materials wherein a fiber pulp suspension is adjusted to a pH in the range of 7.5 to 11.0 with addition of a water soluble calcium compound used in an amount of from 0.5 to 2 weight percent based on the dry fibers weight. The aqueous suspension is maintained at an elevated temperature and is then admixed with a homogeneous mixture of substantially saturated fatty acid salts and a water soluble cationic material. The cationic material is present in an amount of from 0.1 to 5.0 weight parts per weight part of said fatty acid salts. Prior to or subsequent to the admixing step, a precipitating agent is added for providing ions of aluminum, ferric and/or chromic compounds. The fatty acid radicals of

FATTY ACID SALTS

$$\text{(1)} \quad \text{KOH} + \text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_{17}\text{H}_{35} \xrightarrow{\Delta} \text{K}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_{17}\text{H}_{35} + \text{HOH}$$

Stearic Acid Salt of sizing stock

Approximately stoichiometric amounts of the reactants may be employed for the reaction and temperatures of approximately 200° F. must be employed along with a quantity of water. Such temperature and concentration are sufficient for the fatty acids to be saponified by the potassium hydroxide. The sizing stock or fatty acid salt may be formed by reacting the fatty acids with sodium hydroxide or with ammonium hydroxide with nearly equal results in the final sizing process.

As set out in the opening statements, the sodium salts of the fatty acids are insoluble at temperatures in the range of 130–140° F. and, hence, cannot be used alone in the sizing process. The presence of the water soluble cationic materials enables the use of such sodium salts in much the same manner as the potassium and ammonium salts of the fatty acids when used in conjunction with the water soluble cationic materials.

The fatty acid employed may be any one or a mixture of the fatty acids having from 12 to 20 carbon atoms either in chain or the isomeric forms thereof. The saturated fatty acids, such as lauric-C₁₂, tridecylic-C₁₃, myristic-C₁₄, pentadecylic-C₁₅, palmitic-C₁₆, isopalmitic-C₁₆, margaric-C₁₇, stearic-C₁₈, nondecylic-C₁₉, arachidic-C₂₀, are all capable of being used for preparation of sizing stock as they are the more abundant saturated acids of the broad workable group. The unsaturated fatty acids, such as myristoleic, palmitoleic, oleic, linolenic and linolic, may be used in proportions such that the total unsaturated fatty acid radical content is not so great as to be detrimental to the alkaline resistances when such is desired. This limit is 30% by weight. That is, that the weight amount of the fatty acids having unsaturated radicals therein is not more than 30 parts by weight of 100 parts by weight of total fatty acids in the sizing stock. An unsaturated radical content below this upper limit is necessary to attain good alkaline resistivity in the sized products but is not necessary to follow if the other, less critical, but valuable sizing properties are to be attained by the process. The 30% unsaturated limit is known by the inventor from the above prior alum precipitation processes employing the fatty acids.

These fatty acids have non-substituted straight carbon-hydrogen groups which allow for a closely controlled final product. Other isomeric forms of these acids are equally employable and therewith shorter than 12 carbon atoms in the straight chains are encompassed in the invention, such as the isomeric forms of lauric acid.

Various mixtures of these fatty acids may be commercially obtained and therein usually contain some proportion of unsaturated fatty acid radicals. As stated above, this proportion should not exceed 30% unsaturated fatty acid where alkaline resistance is desired and preferably, for highest alkaline resistivity, should not contain greater than 7% unsaturated fatty acids. Various commercially obtainable fatty acid mixtures are marketed by Armour Industrial Chemical Company under tradenames: Neo-Fat 18-S, Neo-Fat 18, Neo-Fat 18-58 and Neo-Fat 58-59; and Darling and Company under tradenames: Dar-Hy, Dar-C and Dar-S77. These commercial mixtures are generally low in unsaturated fatty acid content and contain greater than 80% of at least one or a mixture of stearic, palmitic, margaric and myristic acids. For example, Neo-Fat 18 is commercially pure stearic acid having an iodine value of 1.0. Neo-Fat 185 is C.P. grade stearic acid having an iodine value of 0.5. Neo-Fat 18-58 is a hydrogenated tallow acid having an iodine value of 0.5. Dar-HY and Dar-C are hydrogenated tallow fatty acids having iodine values of 1 and 5, respectively.

As set out above, the percentage of the fatty acids which are unsaturated is only necessary to be controlled within fairly low values if the sized fiber article is to have alkaline resistivity as one of its properties. For the production of sized fiber articles having water, alcohol-water solution, and liver blood resistance, these limits are much less critical and, therewith, mixtures of fatty acids containing high proportions of the unsaturated fatty acids may be employed. The strength and internal bond properties of the fiber products are nearly the same whether saturated or unsaturated fatty acids are employed. Thus, for total sizing properties, excluding alkaline resistivity, other unsaturated fatty acids in high proportion may be employed.

The sizing stock may be prepared by stirring 40 weight parts of such fatty acids as are above set out into a solution of 450 weight parts of water and 10 weight parts of

KOH and then heating for 5 minutes at 210° F. This amount of KOH allows an excess to be present over that stoichiometrically necessary for complete reaction of the stearic acid. This excess tends to drive the Equation 1 to the right by mass action and also allows some free hydroxide present in the sizing stock by which the pH of the fiber suspension to which it is later added may be increased and made more alkaline. The preferred reactant proportions are 5 weight parts acid to 1 weight part hydroxide reactant.

The sizing salts prepared in this manner are then added to an aqueous solution of a water soluble cationic material to make the size of the present invention. The two water solutions are preferably added together at an elevated temperature and vigorously agitated to assure homogeneity.

CATIONIC MATERIAL

The cationic material for making up this sizing stock must be water soluble and may be taken from the class of cationically modified starches or gums and hydrogen-bonding starches and gums. The latter, while not technically classified as cationic materials, behave in a very similar manner in the sizing stock of this invention.

The first group of cationic materials which may be employed are those mentioned above as being cationically modified starches and gums. These materials are known to the art to be those produced by modifying naturally occurring starches and gums so that they exhibit a cationic charge, i.e., a positive charge, when in aqueous medium. Due to the cationic character of the modified starch or gum molecules or aggregates of molecules, the starches are more readily soluble in cold water, as well as being completely soluble in hot water. One such modification of naturally occurring starches and gums may be accomplished according to U.S. 2,813,098, issued to Caldwell and Wurzburg. According to this method, any of the large number of starches (amylaceous substances) may be reacted with an etherification reagent which has the characteristic of reacting with hydroxyl groups of the starch through an ether linkage to introduce a tertiary amino radical into the starch or gum molecule or aggregate of molecules. The etherification agents may be such compounds as dialkyl amino alkyl epoxides or dialkyl amino alkyl halides used in an amount of from 0.5 to 30% based on the weight of the amylaceous substance. The compounds employed may also be the hydrochloride salts of these types of compounds. When such salts are employed, the modified starch may be referred to as a quaternary ammonium salt derivative of the starch or gum base employed as an initial reactant.

The starches which may be synthetically modified to attain a cationic character may be any of these obtained from the vegetable kingdom in grains and tubers. Such hexoses consist of a water-dispersible portion of amylose and a less dispersible fraction known as amylopectin in relative proportions of approximately 20:80, respectively. Such starch may be from the following sources: potato, corn, arrowroot, rice, tapioca, maize, sago and wheat, as well as the hydrolized dextrinized, esterified, oxidized and etherified derivatives of these and other similar starches. These various starches may be converted to a cationically modified form in a granular state, i.e., the ungelatinized state, by employing the teachings of the above patent or in a gelatinized state according to U.S. Patent 2,917,506 to Caldwell and Wurzburg. This latter patent employs similar etherification agents to the first-mentioned patent.

Another cationically modified starch which may be employed is that marketed under tradename Q-TAC Cationic Starch by Corn Products Sales Company. The starch employed may be any of the commonly used amylaceous substances. These are modified by reacting the starch with the reaction product of epihalohydrin and a tertiary amine or a tertiary amine salt. This reaction is described further and in detail in U.S. Patent 2,876,217.

Many cationically modified starches and gums are available in the present market which may be employed for use in the sizing stock for sizing fibers according to the present invention. A cationically modified galactomannan guar gum is marketed by Stein, Hall and Company, Inc., under the trade name Draybond II. Another similarly cationically modified material is a cationic pearl cornstarch marketed by National Starch and Chemical Corporation under the trade name Cato 8. A cationic potato starch which is acceptable is marketed by A. M. Menickle and Sons, under the trademark Epic-N. Many other trademarked materials are currently available which are the products from the reaction of naturally occurring starches and gums with an etherification agent as set out in the above process statements.

The cationically modified gums which may be employed in the present invention may be synthetically modified according to the same processes as the starches. Gums are chemically mixtures of pentoses and hexoses which, in certain environments, behave similarly to starches. Both are classified as polysaccharides, differing in the number of monosaccharide units joined through oxygen atoms in glycosidic type linkages. Such gums may be the naturally occurring varieties, such as locust bean gums, guar gums, and other of a similar nature. Generally, the gum family is classified in three parts: (1) exudates from vegetable saps such as arabic, karaya, tragacanth, ghatti, talha, mesquite, angico and shiraz gums, (2) seed extracts from such as guar, locust bean, quince and psyllium plants, and (3) seaweed products, such as agar, Irish moss, kelt and alginates. These may be rendered cationically modified by subjecting them to etherification reactions in the same manner as in the above patents.

While such cationically modified starches and gums have been suggested for use to increase the effectiveness of paper sizing processes, they have not been suggested previously for use over specific weight ranges with saturated fatty acid salts and their conversion to insoluble soap sizing. Hence, while such materials have been known for inclusion with paper pulps, the specific manner of inclusion in the sizing of the present invention does not appear.

Due to the presence of the positively charged groups or cationic groups, the above cationically modified starches and gums have the property of exhibiting cationic activity. Any modified starch or gum which exhibits similar or equivalent cationic activity to the above materials may be used as the cationic material of this invention.

The broad designation of cationic materials which may be employed with the fatty acid salts to make up the sizing stock of the present invention also includes hydrogen-bonding starches and gums.

Such materials may be extracted from their respective vegetable origins and used directly, as such, they may be referred to as naturally occurring hydrogen-bonding starches and gums. Other non-hydrogen-bonding gums may be rendered so active by chemical treatment.

The naturally occurring materials are characterized in that there are numerous hydroxyl groups on the monosaccharide units and these are sterically arranged so that hydrogen-bonding occurs between the chains. Such hydrogen-bonding is generally attributed to the presence and behavior of these hydroxyl groups. Such naturally occurring materials as locust bean gums and guar gums can be employed without a chemical modifying treatment. A preferred material of this type is tamarind seed flour, which while being inexpensive in the present market, is extremely effective for sizing over wider pH ranges and for attaining greater sizing properties in the final paper product. A chemically modified starch known as dialdehyde starch may also be employed as it contains sufficient hydrogen-bonding activity. It is produced by treating ordinary native starch with periodic acid or dichromate. Generally, sufficient hydrogen-bonding activity is necessary to attain solubility in an aqueous medium at temperatures of 90 to

130° F., and this activity may be either naturally occurring or attained by chemical treatment.

Many naturally occurring hydrogen-bonding starches and gums have been extracted and isolated from the vegetable matter in which they are found in nature. The above preferred hydrogen-bonding material having cationic-type properties is a gum which is referred to in the art as tamarind seed flour, which term identifies its origin as being from the tamarind plant. This extracted and purified gum is composed of galactose, xylose and glucose units in the approximate molar ratio of 1:2:3. The tamarind gum has a typical analysis as follows, expressed in percentage ranges—

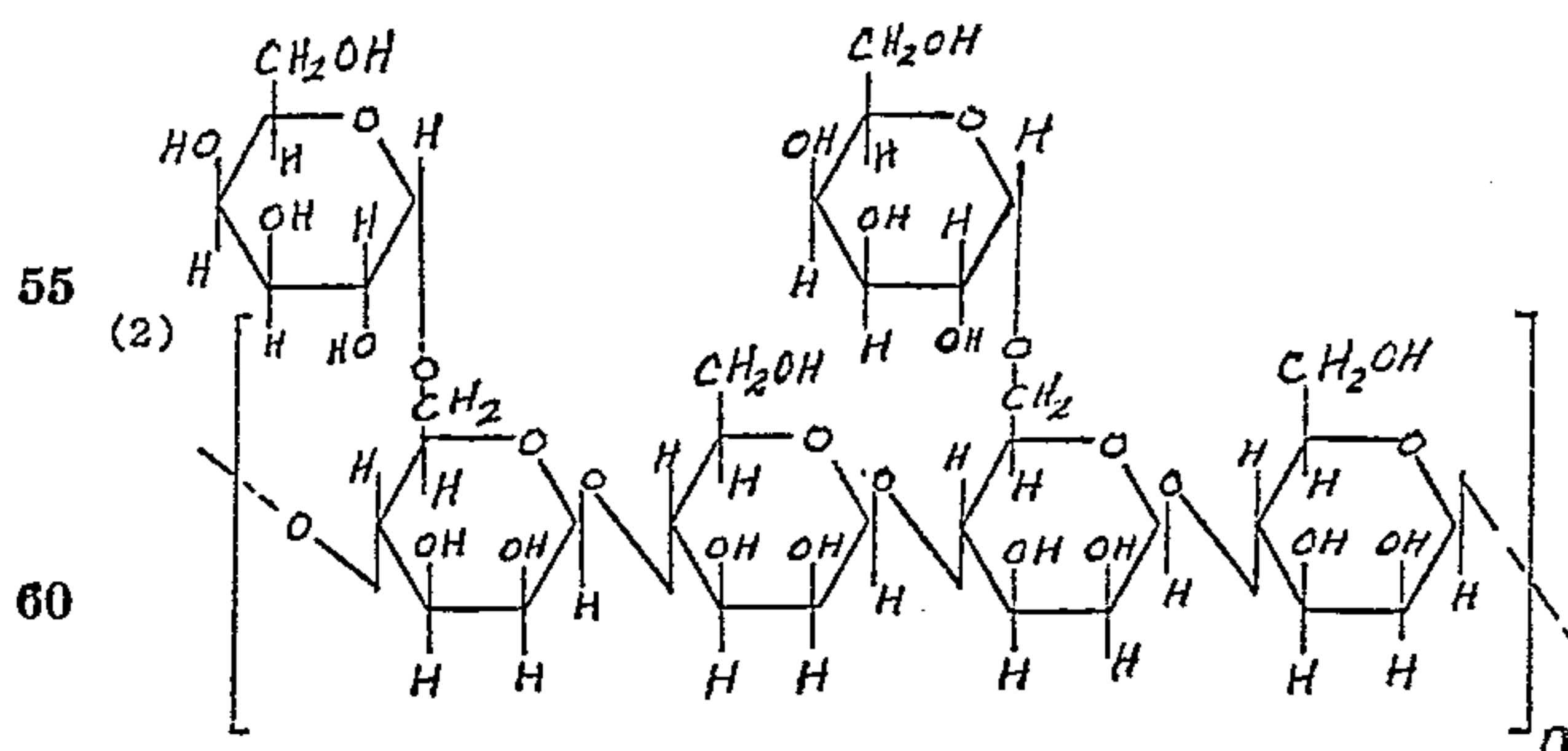
Constituent:	Weight percentage range
Moisture	5.0–12.0
Ash	2.3–2.5
Protein	16.0–18.0
Acid insolubles	9.0–13.0
Fats	6.0–7.0
Gum content	49.0–58.0

Such a seed flour may be obtained from Dycol Chemicals, Inc., under tradename Dycol D-16. Another source of the seed flour is Keygum Mark IX marketed by American Key Products, Inc. An analysis for this gum is—

Constituent:	Percent by weight
Protein	17.67
Fat	7.00
Acid insolubles	9.50
Ash	2.50
Moisture	5.04
Base gum	58.50

While tamarind seed flour as it naturally occurs contains proteinaceous and fat materials, these are not objectionable in the percentage in which they occur.

Another hydrogen-bonding gum is that obtained by extraction from the guar plant. This gum is the principal component of *Cyamopsis tetragonolobus*, a leguminous seed. The gum is essentially a straight chain mannan branched at quite frequent intervals with single membered galactose units on alternate mannose units. The mannose units are, in turn, linked to one another by means of beta (1-4) glycosidic linkages. The galactose branching is accomplished through an alpha (1-6) linkage. Hence, it is chemically classified as a galactomannan but may also be classified as a high molecular weight carbohydric polymer or polysaccharide made up of many mannose and galactose units linked together in the pattern described. As such, the guar gum molecule has the type formula of:



Such a guar gum is extracted from the guar plant and has a typical analysis of—

Constituent:	Weight percentage
Galactomannan content	78–82
Protein	4–5
Crude fiber	1.5–2
Ash	0.5–0.9
Ether extract	0.5–0.75
Arsenic	0
Heavy metals	0
Iron	trace
Moisture	10–13

This guar gum will hydrate and swell in either hot or cold water and exhibits hydrogen-bonding activity as the molecular structure illustrated by Formula 2 shows the presence of numerous hydroxyl groups. Thus, the basic straight-chain structure of the guar gum molecule along with the regularity of the single member galactose branches, result in a gum product that exhibits unusual effects which, for purposes of the present invention, are similar to the effects of the chemically modified cationic starches and gums. While this guar gum may be employed in the present invention as the cationic material which is mixed with the sizing stock, it may also be chemically treated to attain a cationic charge such as by the above synthetic etherification processes. Thus, the gums and starches which occur naturally and have hydrogen-bonding activity may be converted through an etherification process to a true cationically modified product which has, in addition to the hydrogen-bonding activity, the cationic properties of the above cationically modified materials.

Guar gums in the unmodified form, as well as those in cationic form, are marketed by Stein, Hall and Company, Inc., under the trade name Jaguar.

Locust bean gum may also be employed as a hydrogen-bonding, naturally occurring galactomannan. It is similar to guar gum in that both are galactomannans having a straight mannan chain linked through beta (1-4) glycosidic linkages. The primary difference is that the galactose branchings are less frequent than on the guar gum molecule set out above. As a result, the locust bean gum is not as dispersible in cold water, but must be cooked to attain a usable condition for inclusion into the sizing stock.

The general requirement for the hydrogen-bonding starch or gum used is that it have hydrogen-bonding activity approximately equivalent to the specifically named substances.

From the above listing of cationic starches and gums and hydrogen-bonding starches and gums, it can be seen that any of the broad class named may be employed in the sizing suspension of the present invention. The cationic treatment given to the naturally occurring and ordinary starches and gums should be so that cationic groups in amounts of at least approximately 2% by weight are inserted into the starch and gum. These groups may result from reacting the starch with from 0.5 to 30% of the etherification reagent on the basis of the weight of the starch. For the hydrogen-bonding gums, they should have sufficient hydrogen-bonding activity to remain soluble at the 90-130° F. temperatures employed in the paper-making machine.

The relative cost of these materials, in the present market, is important for establishing the most economic operation of the invention. Tamarind seed flour can be obtained, as mentioned above, for approximately 12 cents per pound. The chemically modified starches and gums range from approximately 2 to 5 times this cost; therefore, the additional chemical treatment necessary to render non-hydrogen-bonding starches and gums cationic in behavior is expensive, but may be used economically, for particular grades of paper.

The sizing stock is made by adding sodium, potassium and/or ammonium salts of the fatty acids, plus any excess KOH which may be present in the aqueous mixture, to a water suspension of the cationic material in proportions such that the amount of the cationic material to the weight of the salts of the saturated fatty acids is between the proportion limits of 0.1:1 to 5.0:1. Below the lower limit of the cationic material range the unique effect of the presence of this material is curtailed, while above the upper limit is not believed to be critical and can be increased somewhat. The dilution of the sizing stock and the water suspension of the cationic materials is such that the final size solution contains approximately 4.0% fatty

acid salts and 1.5% cationic material, in the preferred proportions.

The acid salts and the pulp stock may be added to one another and then followed by the addition of the cationic material or alternatively, the cationic material may be added first to the pulp stock and then followed with the addition of the sizing acid salts. The preferred manner of addition is to premix the cationic material with the fatty acid salts to form the sizing stock and thereafter to add it to the pulp stock as it is being moved through the paper-making machine and onto the forming wires. This premixing may be simultaneously with addition to the pulp suspension. The sizing stock is not believed to be in an emulsion form and, therefore, special high speed mixing and stable storage conditions are not necessary.

PRECIPITATION AGENT

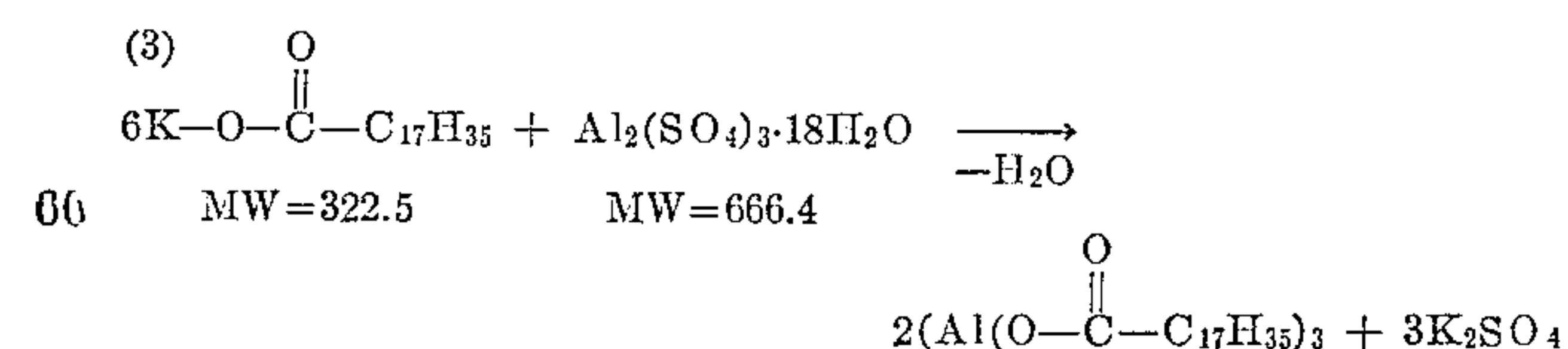
The precipitating agent which is employed for setting the saturated fatty acids as insoluble soaps which act to size the pulp, must provide metallic ions which are polyvalent. In order to provide the ions, the precipitating agent must be soluble at the temperatures of the sizing process. The polyvalent metallic ions may be aluminum, ferric or chromic. Such ions can be released from the following group of precipitating agents: aluminum sulfate, aluminum chloride, potassium sulfate, aluminum sulfate salts, ferric sulfate and chromic sulfate. Any common water soluble salts of these anions are usable. The aluminum sulfate and potassium sulfate-aluminum sulfate salts are normally referred to as alums. The alum employed may be anhydrous alum, $\text{Al}_2(\text{SO}_4)_3$; papermakers alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and common alum,



When the term ("alum" is employed in the working examples, below, papermakers alum is intended.

The precipitating agents thus set out may be added at any of the commonly employed points of addition in paper mills. One of the most convenient points of addition is the wire pit sump of the primary suspension. Another is the fan pump of the primary or secondary pulp suspensions. Generally, the premixed final sizing solution may be conveniently mixed into the machine boxes or into the fan pumps.

The amount of the water soluble precipitating agent which is controlled according to the amount of the sizing stock and cationic material used may be varied. The precipitating agent is added in an amount which will create an excess of polyvalent metal ions in solution, over the amount which would be required for a stoichiometric reaction to precipitate the insoluble soap sizing. The excess of the precipitating agent employed may best be explained by reference to an illustrated metathesis reaction of the type which occurs during the sizing in the present invention. Equation 3 below illustrates the reaction of papermakers' alum with potassium stearate.



Thus, the stoichiometric ratio for entering reactants is 6/1. The reactants are employed according to the present invention in molar ratios of approximately 0.6/1. The usable weight range is from 1 to 12 lbs. of papermakers alum per lb. of fatty acids salts. It is believed that this excess of the precipitating agent drives the metathesis reaction to the right by the mass action principle to form the tristearate and thus results in the formation of very little mono-stearate and distearate soaps. As a practical matter, it is nearly impossible to assure that no mono- and di-stearate soaps will be present in the sizing, but their presence is considerably minor and, therefore, the

result of the reaction may be viewed as being the formation of the tristearates and tripalmitates, etc.

It is believed that the excess of the precipitating agent aids in attaining the valuable sizing properties for the materials of the present invention. Further, the use of the high precipitating agent concentration allows a higher alkalinity resistivity to be established in the finally sized fiber product.

By structural formulas, the precipitating agent may be any of the following: $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$,

$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, AlCl_3

$\text{Fe}_2(\text{SO}_4)_3$ and $\text{Cr}_2(\text{SO}_4)_3$

PULP STOCK

The pulp suspension which is to be sized by the sizing stock, together with the precipitating agent, may be made up with refined fibers such as: bleached and unbleached fibers, ground wood, soda pulp fibers, semi-chemical fibers, kraft fibers, sulphite fibers, textile and synthetic fibers, such as viscose rayon and cellulose acetate, and other cellulosic fibers. The pulp may be first refined in Jordan engines to an acceptable fiber length. Such refining is measured in the ability of water to drain therefrom and is measured in the industry by terms of Canadian Standard Freeness. Values of from 300–600 cc. Canadian Standard Freeness are normal and vary upon the type of paper and the primary or secondary layer thereof. Further, the pulp consistency can normally be employed at approximately 0.53% by weight, although considerable variation is possible for consistency.

Most pulp suspensions, particularly the unbleached pulps, prior to refining, have alkaline pH's, which for ordinary rosin sizing, must be lowered by the addition of alum to approximately 4.5 to 5.5 after sizing. This addition of alum, in order to lower the pH for the sizing reaction, weakens the fibers. An advantage of the present invention is that it provides a sizing process which may be carried out at higher pH's even above those which result after the refining of the pulp. Thus, the weakening of the fibers by setting the size on the acid side of 7.0 pH as in normal sizing processes has now been eliminated.

The normal pH's of pulp suspensions after refining, of approximately 7.0–8.0, may be adjusted by either additional basic material or acidic material to a wider pH range of from 5.0 to 11.0. Over this wide pH range, sizing can be obtained which is completely unexpected, both in rosin sizing processes, fortified rosin sizing processes, and in those sizing processes in which fatty acids are precipitated in the form of insoluble soaps, but wherein there is no cationic or hydrogen-bonding material present in the stock suspension or wherein such materials are employed only in amounts and by practices dictated by the addition of small quantities of starches and gums in the past paper-making practices. The ability to size at the higher pH's is an unexpected result and allows attainment of higher physical strength for the paper products sized according to this invention.

A further pre-treatment of the pulp stock is that a water soluble calcium salt can be used to raise the final formation to a value in the range of 7.5 to 11.0. Generally, it is believed necessary to have calcium ions present when the fatty acid salts are precipitated at formation pH's greater than 7.5 and when high alkaline resistivity is to be a property of the product. For sizing at precipitation pH's in the range of 5.0 to 7.5, no such pre-treatment is believed necessary or desirable. Thus, for the attainment of general sizing properties, the setting of the size may be accomplished over the entire range of final formation pH's and alkaline resistance may be imparted to the fiber product at pH's of 5.0 to 7.5 without the use of calcium salts. As the preferred final formation pH range is from 6.7 to 6.8, the use of such salts is not required for the optimum mode of employment.

The use of alkaline pH's for the pulp stock is important in that lower refining power is required and the entire paper machine output can be increased as the pulp can be refined quicker. It is impossible to refine pulp at or below 7.0 pH with the low energy expenditure required for the higher alkalinities. The precise effect of the use of calcium salts to raise the pulp pH to a higher value than exhibited after refining is not adequately understood for a theoretical explanation to be advanced. One effect is that the amount of alum required for complete setting of the size is less. Another effect is that the alkaline resistivity of the fiber product is greatly improved when the final formation pH used was above 7.5 and this improvement was noted to increase with the higher pH's which were maintained by increasing amounts of the calcium compound added.

When a final formation pH of between 7.5 to 11.0 is to be used, $\text{Ca}(\text{OH})_2$ can be added to bring the pH to its final value by addition in an amount of from 0.5 to 2 weight percent based on the weight of the dry fibers. The other water soluble calcium salts can be used in lieu of the $\text{Ca}(\text{OH})_2$ and are employed in amounts to furnish the same Ca^{++} concentration as the above amounts of hydroxide. Calcium carbonate, calcium nitrate and calcium chloride may all be used in this manner.

It is notable that only compounds liberating Ca^{++} showed this effect. Thus, water soluble salts of iron, sodium, barium and potassium did not give the effect. Also, it was observed that calcium salts, alone, could be used as the precipitating agent if only alkaline resistivity were desired, to the exclusion of water and alcohol resistance.

For the employment of calcium compounds, it is preferred to add them as a last step, following the treatment of the pulp stock with the excess amount of alum or other precipitating agent. However, the calcium salt or hydroxide may be added as a pre-refining or later step, before the major setting agent is added. As the calcium ions are not detrimental, they may be added to pulp suspensions which are to be sized at pH's below 7.5.

Within the ranges set out for the various materials and operating conditions, paper can be economically sized to attain sizing properties superior to those of the rosin sizes and, by employing a sufficient amount of the sizing stock, a highly alkaline resistant product may be produced. By properly controlling the factors effecting alkaline resistance, extremely valuable paper products may be made by the present invention, which have in addition to the superior sizing properties as measured against the ordinary sizes, an alkaline resistivity equivalent to the more expensive synthetic sizes. Such factors are: (1) the formation pH of the pulp suspension at the time the paper is formed on the paper machine, (2) the ratio of the precipitating agent to the fatty acid salts, (3) the prior treatment of the fibers by the addition of calcium ions, and (4) the temperature of the size and water stock system of the paper machine. These have been treated in the above general description.

The objects set out above, as well as the general description, will be more clearly understood by those ordinarily skilled in the art by reference to the following examples in which parts are by weight unless otherwise specified.

In these examples of practice, certain tests have been conducted on the final fiber products and the results thereof are set out in the various Tables of Data. In order to adequately understand the data which is given for these working examples, the following definitions of those values are set out. In order to standardize the testing procedures, the sized fiber samples were conditioned at 50% relative humidity at 73° F. for 24 hours prior to the testing.

The evaluation tests for the sized products were:

(1) Caustic drop test.—Dropping a single drop (0.05 cc.) 5% NaOH onto the product surface from a distance

of 2 inches and recording the time for the drop to be completely absorbed into the paper.

(2) Water drop test.—Dropping distilled water in the same manner as in (1) and recording the time in seconds for a single drop to be absorbed.

(3) Alcohol drop test.—Dropping 25% grain alcohol solution in the same manner as in (1) above and recording the time in seconds. A single drop (0.025 cc.) was employed.

(4) Water immersion test.—The gain in weight in centigrams, by a 6 x 6 inch sample of product resulting from a 10-minute immersion in 73° F. water after excess water has been blotted off.

(5) Liver blood test.—The time in hours recorded for a bloodstain to penetrate one thickness of the product when a 1½ x 1½ inch piece of fresh pork liver is placed thereupon. A thickness of the material is considered to be the total thickness, comprised of both the primary and secondary stock layers.

(6) Bursting strength of paper.—Evaluated by TAPPI Standard-T 403 ts-63.

(7) Cobb test.—Evaluated according to TAPPI Standard-T 441 os-63.

(8) Elmendorf tear.—Evaluated according to TAPPI Standard-T 414 m-49.

(9) Internal bond test.—The reading from a Hinde and Dauch Crush Tester Gauge (TAPPI and ASTM standards). The test was conducted by placing a 1½ x 1½ inch sample between two pieces of double coated pressure sensitive tape. The sample is placed between opposing U-blocks having the legs of each U-block meshed with one another so that a rectangle is formed and the assembly clamped together with a press. The assembly is then placed between platens of a Hinde and Dauch Crush Tester. The gauge dial is recorded at the time of separation or movement of the U-blocks with respect to one another. This is a test of the internal bond strength of the fibers and a higher bonding is identified by a higher gauge reading.

(10) Photovolt brightness.—Recorded by a photovolt brightness tester—Photovolt Corp.

Example I

A series of handsheets were made in which the pounds of alum per pound of saturated fatty acids were varied from 0.6 to 20.0 in order to attain a range of final formation pH's. The runs were made using potassium, sodium and ammonium salts, both with and without a cationic material. The results of these runs according to the above testing data are set out in Table 1.

In order to further vary the pH's of the pulp suspensions prior to addition of the sizing stock, various soluble metal salts and sodium hydroxide, as well as dilute sulfuric acid, were employed to adjust the pH's to those desired, in order to attain a gradual variation in the final formation pH.

The handsheets were made by first suspending unbleached kraft fibers in water at a consistency of 0.53% and then refining to 640 cc. Canadian Standard Freeness and then taking 10 grams of the pulp on a dry basis for use in making a handsheet in a Noble and Wood Handsheet Mold. The pulp suspension after refining showed a pH of 7.8. The various amounts of alum shown were then added to ready the pulp suspension for the addition of the sizing stock. The sizing stock was then added and the aluminum ions of the alum precipitated or set the insoluble soap sizing. The handsheets were then made on the mold and passed through a wringer and dried on Noble and Wood drying drums at 40 p.s.i. steam pressure. The handsheet produced was then conditioned at 50% relative humidity at 73° F. for 24 hours and then the testing carried out and the values shown in Table 1 recorded.

In this example, all of the handsheets produced were made by a 0.375 part by weight addition of sizing fatty

acid salts (calculated on the free fatty acid weight) per 100 parts by weight of dry fibers. The cationic material was present in an amount of 7.5 weight parts per 20 weight parts of entering fatty acids or 0.14 weight part per 100 weight parts of fibers.

The following description is set out due to the fact that the handsheets made according to this example were sized with all of the sizing salts set out in the present invention, namely, the potassium, ammonium and sodium salts of the saturated fatty acids, both with and without cationic materials. The handsheets of the A series are those prepared with the potassium salts of the fatty acids. The runs with B notation are those prepared with sodium salts, while those with C notation are those of the ammonium salts. Further, the run numbers of the (1) series are without a cationic material while those of the (2) series are with a cationic material.

The sizing salts for the examples were prepared by mixing 476 parts by weight of water with 4 parts by weight of the potassium hydroxide, sodium hydroxide or ammonium hydroxide and then adding in 20 parts by weight of saturated fatty acids mixture and agitating the resultant mixtures and heating for approximately 5 minutes at 210° F. The sizing salts mixtures were then cooled to 150° F. prior to using. The fatty acids employed for making the sizing stock had a gas chromatography analysis as follows—

Fatty acid:	Percent by weight
Lauric -----	0.5
Myristic -----	6.9
Pentadecylic -----	0.1
Palmitic -----	18.9
Margaric -----	0.5
Stearic -----	73.1

These fatty acids have an iodine value of 1.9 which indicates the total unsaturated acid portion is 2%. The acid value is 201 and the titer °C. is 61.5 (the initial solidifying temperature). Such a mixture of fatty acids is highly acceptable as the unsaturation content is lower than 30% and also lower than the preferred 7%. A mixture of saturated fatty acids of this analysis is marketed by Armour Industrial Chemical Company under the tradename NEO-FAT 18-59.

The sizing stock for series (1) consisted of the saponified fatty acids, together with any excess hydroxide which was not required for the complete metathesis reaction. Those handsheets sized by series (2) contain in addition to the fatty acid salts a tamarind seed flour in small proportion. The tamarind seed flour employed is that set out above as marketed by Dycol Chemicals, Inc., New York, N.Y., under the trade name Dycol D-16.

A further detailed description of the method of making the handsheets according to this example is as follows:

1-A. The sizing stock was made up with 476 parts water, 4 parts KOH and 20 parts of the above fatty acids by heating them to 210° F. for about 5 minutes. The handsheets were then made at final formation or precipitation pH's of: 4.2, 5.0, 5.5, 6.0, 6.5, 7.0 and 7.5. After refining of the pulp stock, the pH was 7.8 which was then raised to 8.0 with NaOH. Thereafter, the aluminum sulfate solution was added for the various pH adjustments, the alum being acidic in aqueous media. After the alum treatment, the size was added to attain a sizing of 0.375 weight percent measured as original fatty acids and based on the weight of dry fibers.

1-B. The handsheets were sized exactly as in the handsheet made with KOH with the exception that NaOH was employed as the saponifying hydroxide for the fatty acids.

1-C. The above handsheet manufacture was repeated employing a sizing stock made in the same manner from 473 parts water, 7 parts of concentrated ammonia hydroxide and 20 parts of the above fatty acids.

2-A. The same type of handsheets was made as in 1-A with the exception that the sizing stock used was made by heating 468.5 parts water, 7.5 parts tamarind seed flour, 4 parts KOH and 20 parts fatty acids to 210° F. Thereafter, the pulp treatment with alum and the precipitation and handsheet formation were as above.

2-B. The same procedure was followed as in 2-A with the exception that NaOH was employed rather than potassium hydroxide.

2-C. The sizing stock for this group of handsheets was made by heating 465.5 parts of water with 7 parts concentrated ammonia hydroxide and 7.5 parts tamarind seed flour and 20 parts by weight of fatty acid to about 210° F.

In order to obtain comparisons with both ordinarily sized products under similar conditions and products sized with alkaline resistance, synthetic sizing under similar conditions, the following experiments were run: 3—a fortified rosin sizing was used in the same 0.375% treatment based on the dry fibers with sufficient aluminum to precipitate the same and to obtain a pH of 5.5 prior to formation; 4—a handsheet was made with an expensive commercially available alkali resistant sizing which was used by first adjusting the 0.53% consistency pulp suspension to 7.0 pH and then adding size to a 0.25% treatment. No alum is required to precipitate this synthetic alkaline resistant sizing.

The test data obtained from their series of handsheets is set out in Table 1, below.

TABLE 1

Run No.—Sizing Stock	pH Prior to Sizing Stock Addition	Lbs. Alum Per Lb. Fatty Acid	Final Formation pH	5% NaOH Drop Test (Avg. Sec.)	Water Drop Test (Avg. Sec.)	25% Grain Alcohol Drop Test (Avg. Sec.)
1-A.—K plus salt of fatty acids.....	4.0	20.0	4.2	12	4,366	1,408
	5.0	9.6	5.0	16	4,476	2,006
	5.5	6.2	5.5	155	5,111	2,020
	6.0	4.9	6.0	1,200	4,368	1,877
	6.5	3.2	6.5	616	4,870	1,371
	7.0	2.3	7.0	290	4,745	887
	7.5	0.6	7.5	8	11	4
1-B.—Na plus salt of fatty acids.....	4.0	20.0	4.2	13	4,524	1,814
	5.0	9.6	5.0	16	5,173	2,060
	5.5	6.2	5.5	35	4,888	1,860
	6.0	4.9	6.0	145	4,620	1,914
	6.5	3.2	6.5	579	4,235	1,600
	7.0	2.3	7.0	123	4,153	883
	7.5	0.6	7.5	9	1,200	10
1-C.—NH ₄ plus salt of fatty acids.....	4.0	20.0	4.2	8	4,739	1,784
	5.0	9.6	5.0	14	4,743	2,089
	5.5	6.2	5.5	70	4,672	1,850
	6.0	4.9	6.0	1,920	4,400	1,858
	6.5	3.2	6.5	1,291	4,157	1,342
	7.0	2.3	7.0	102	3,837	797
	7.5	0.6	7.5	21	1,611	4
2-A.—K plus salts plus cationic material.....	4.0	20.0	4.2	10	4,257	1,871
	5.0	9.6	5.0	10	5,398	2,554
	5.5	6.2	5.5	25	4,454	2,004
	6.0	4.9	6.0	802	4,326	2,070
	6.5	3.2	6.5	3,002	4,238	1,796
	7.0	2.3	7.0	3,066	4,369	1,764
	7.5	0.6	7.5	2,440	3,835	1,212
2-B.—Na plus salts plus cationic material.....	4.0	20.0	4.2	9	3,976	1,676
	5.0	9.6	5.0	18	4,168	1,913
	5.5	6.2	5.5	1,322	4,491	1,756
	6.0	4.9	6.0	2,730	4,054	1,730
	6.5	3.2	6.5	2,297	4,264	1,564
	7.0	2.3	7.0	1,154	3,570	14
	7.5	0.6	7.5	255	8	3
2-C.—NH ₄ plus salts plus cationic material.....	4.0	20.0	4.2	14	4,112	1,875
	5.0	9.6	5.0	15	4,216	1,788
	5.5	6.2	5.5	333	3,805	1,525
	6.0	4.9	6.0	920	3,619	1,266
	6.5	3.2	6.5	1,403	3,552	1,120
	7.0	2.3	7.0	456	2,579	9
	7.5	0.6	7.5	57	8	4
3.—(Fortified rosin).....	5.5	9.6	5.5	50	4,595	1,907
4.—(Synthetic sizing).....	7.0	None	7.0	2,193	4,584	1,701

As a general rule for interpreting the alkaline drop test data set out in Table 1, and elsewhere, an acceptable value for the average absorption time for both sides of the paper is 300 seconds. This measurement indicates that the times for a drop of 5% NaOH to complete penetration into the secondary layer of the paper and into the primary layer of the paper have been averaged to a value of 300 seconds or 5 minutes.

Using this test for acceptable alkaline resistivity data, it can be seen that in runs 1-A, acceptable values are found when the final formation pH is from 6.0 to 7.0.

This is a pH range and the NaOH drop tests show values equal to up to approximately four times that which is an acceptable value. The runs 1-B show only one acceptable alkaline resistivity test at 6.5 pH which is low. Essentially, there is no alkaline resistivity in this run conducted with the sodium salt of the fatty acids in absence of a cationic material. The soda salt balled and clumped even at the elevated temperatures employed in the handsheet mold. Runs 1-C showed two acceptable alkaline resistivity measurements at 6.0 and 6.5 pH's, respectively. In none of the series 1 runs were acceptable alkaline resistivities attained over a wide range of final formation pH's.

The series 2 runs generally show much higher alkaline resistivity and over a greater range of final formation pH's. Also, the data shows that sizing can be accomplished at from about 5.5-6.0 pH to as high as 7.5 pH which is completely unexpected, based upon experience in the rosin and fortified rosin sizing processes. Further, run 2-B shows that the sodium salts of the fatty acids can be adequately employed for attaining high alkaline resistivity in paper when the sizing stock contains therein a cationic or hydrogen-bonding material, such as the tamarind seed flour employed. Thus, the inability to use such sodium salts of the fatty acids has now been overcome in this rather unexpected manner by the use of the cationic materials within the specific proportions set out herein.

By runs 2-A, it is seen that the use of the cationic ma-

terial increases the pH range over which the materials may be sized and greatly increases the alkaline resistivity of the preferred potassium salts of the fatty acids.

The cationic material addition in the sizing stock makes the stock easier to handle in that a single addition to the pulp may be effected for creating the sizing, thus being includable in the same manner as the ordinarily employed rosin and fortified rosin size materials. It should be noted that with the inclusion of the cationic material, alkaline resistivity values for both the potassium and sodium salts are greatly increased over those without the material

present. Further, the ammonia salts of the fatty acids when used alone have acceptable values only over a very narrow pH range of 0.5 but have acceptable values, although lower, over a pH range of from 5.5 to 7.0 when the cationic material is added. The overall effect of the cationic material is to increase the alkaline resistivity over a greater final formation pH range.

That the increase in effectiveness of the size is not obvious can be seen from the increases in alkaline resistivity gained by employing the cationic materials. For the potassium hydroxide, the increases are on the order of 300 to 400% while the values for the sodium hydroxide salts are much greater than these values.

Run 3 made with the fortified rosin sizing shows practically no alkaline resistivity, but does have good water resistivity. A comparison of the water drop test data and the grain alcohol test data with values attained for the fortified rosin sizing shows that in most runs the sizing material of the present invention gives equivalent results to those attained by the fortified rosin sizing, as well as to those for the commercially available synthetic alkaline resistivity sizing. Obviously, the amount of insoluble soap sizing in the products produced by this invention can be decreased to a point where the alkaline resistivity is on the order of that obtained in the fortified rosin sized products, but wherein the water and alcohol resistivity is of the same order. This is particularly significant in that for low sizing concentrations the size of the present invention is economically competitive with rosin and fortified rosin sizing for sizing bulk paper, such as bag paper, and various grades of kraft papers. At a sizing concentration of the insoluble soap sizing of about 2.0 pounds per ton of paper, measured on the basis of free fatty acids going into the sizing stock, the water resistivity and alcohol resistivity for the present product is approximately equivalent to that of the fortified rosin sized product, while the alkaline resistivity is still superior. This size concentration is 0.1% as compared to 0.375% in the handsheet of this example. When alkaline resistivity is necessary for the paper, this can be attained simply by increasing the concentration of the insoluble soaps to approximately 4.5 pounds per ton of the product (0.225% treatment). It is obvious that a concentration increase of approximately two-fold results in a product which has similar alkaline resistivity to the more expensive synthetic sizing material while it is at the same time much less expensive, being only slightly above the costs of sizing with fortified rosin.

For only water resistivity it can be said from the data of Table 1 that all of the handsheets sized with the salts of the fatty acids, together with a cationic material, show good water resistance up to a formation pH of 6.5. The alcohol drop test is a type of an accelerated water resistance test and can be employed for judging the water-holdout over prolonged periods. These values are also good over the wide pH range employed.

Thus, for general sizing properties, the sizing stock of the present invention may be employed to size bulk produced papers on a basis which is competitive with the ordinarily employed rosin and fortified rosin sizings. Further, the sizing stock may be employed to size papers in higher concentrations of approximately 7.0 pounds per ton of pulp, at which amount a superior alkaline resistivity is present over that attainable by the employment of greatly more expensive synthetic alkaline resistant sizing.

Example II

A series of handsheets were made to illustrate the use of various cationic materials for increasing the alkaline resistivity and sizing efficiency of the potassium salts of the fatty acids over handsheets made with non-cationic starch and gum type additives.

This example illustrates that cationically active or hydrogen-bonding materials are necessary in order to attain

the high alkaline resistivity and overall sizing properties in papers made according to the present invention.

The pulp used to make the handsheets in this example was unleached kraft fibers refined to 530 cc., Canadian Standard Freeness, and having a 0.53% consistency in aqueous water suspension and a pH of 8.0. This pulp suspension was then adjusted to various pH levels with aluminum sulfate solution (3% by weight papermakers alum in water). The treated pulp fibers were then sized by adding a mixture of the potassium salts of a mixture of fatty acids at 0.25 weight percent treatment measured as fatty acids weight and basis on the dry fibers, together with various organic starches, gums and starch derivatives. The fatty acids employed were converted to the potassium salts by heating a mixture of 475.5 weight parts of water, 4.5 parts potassium hydroxide and 20 parts of the fatty acids at 212° F. for 5 minutes with agitation. The pH of the resulting sizing stock was 9.7.

The mixture of fatty acids had a gas chromatography analysis as follows:

Fatty acids:	Weight percentage
Caprylic	0.27
Capric	0.54
Lauric	1.08
Isomyristic	0.41
Myristic	3.39
Myristoleic	Trace
Pentadecanoic	2.3
Isopalmitic	0.54
Palmitic	38.88
Palmitoleic	0.27
Margaric	4.47
Isostearic	0.68
Stearic	43.36
Oleic	3.79

The greatest values are palmitic and stearic. This mixture of fatty acids contained 4.06% unsaturated fatty acids.

For this example, a number of different starch and gum materials, both cationic and non-cationic, have been employed. In order to employ these in making up the sizing stock in the manner best suited to the individual nature of each, specific statements of practice are set out below for each of the series of handsheets made:

(A) The sizing stock above set out was used to size pulp suspensions maintained at 6.9 pH (A) and at 6.0 pH (A-1) by addition of aluminum sulfate solution. No cationic material was present.

(B) A size mixture prepared by mixing together 473 parts water and 2.5 parts of a cationically modified galactomannan guar gum, and heating to 190° F., then adding 20 parts of the fatty acid and 4.5 parts of potassium hydroxide and heating to 190° F. for 5 minutes. The resulting pH was 9.3. The handsheets were made by sizing pulp stocks which were previously adjusted with aluminum sulfate to pH's of 6.9 (B), 6.0 (B-1) and 5.0 (B-2). The guar gum was that obtained from Stein, Hall and Company, Inc., under tradename Draybond II.

(C) A sizing mixture was made by heating 461 parts water and 15 parts of a cationically modified white pearl cornstarch to 190° F., followed by adding 20 parts of the said fatty acid and 4 parts KOH and heating to 210° F. for 10 minutes. The resulting pH was 9.7. Handsheets were made by sizing the pulp suspension previously adjusted to pH's of 6.9 and 6.0 with the addition of aluminum sulfate solution. The handsheets were coded C and C-1. In these runs the cationic starch employed was that known as Cato 8 marketed by National Starch and Chemical Company under the above-referred-to Caldwell and Wurzburg patents.

(D) A sizing mixture was made up by heating 466 parts water and 10 parts of a cationically modified potato starch to 190° F. and thereafter adding 20 parts of the fatty acid mixture and 4 parts of KOH and boiling for

5 minutes at 212° F. The resulting pH was 9.3. Handsheets were made by adding the sizing stock thus prepared to a pulp suspension of 0.53% consistency maintained at 6.9 pH by prior addition of aluminum sulfate. This handsheet was coded D. A like handsheet at 6.0 pH was coded D-1. The cationic potato starch employed was that marketed by A. M. Menickle and Sons Co. under the tradename Epic-N.

(E) A sizing stock was made up by the identical procedure as in paragraph B, above, but wherein the cationic material used is a mixture of a guar gum and a locust bean gum which has not been chemically modified, but is a hydrogen-bonding gum mixture. The pH of the resulting sizing stock was 8.9. Single handsheets were made at 6.0 pH with aluminum sulfate being prior added. The mixture of guar and locust bean gums is marketed by Morningstar-Paisley Company as Gum No. 6910.

(F) The sizing stock was prepared by agitating 466 parts water and 10 parts of a non-cationic white pearl cornstarch at a temperature of 190° F. Thereafter, 20 parts of the fatty acid mixture and 4 parts of potassium hydroxide were added and the resultant mixture was heated to 210° F. for 10 minutes. The resultant pH was 8.7. Handsheets were made at 6.9, 6.0 and 5.0 pH which resulted from the successive addition of larger amounts of aluminum sulfate. These handsheets were coded F, F-1 and F-2, respectively. The ordinary starch employed for this sizing stock is marketed by Anheuser-Busch Company as Pearl Cornstarch No. 7022.

(G) The sizing stock was made up by agitating 456 parts water and 20 parts of a non-cationic thin boiling starch at a temperature of 190° F. Thereafter, 20 parts of the fatty acids and 4 parts of the KOH were added and heated to 210° F. for 10 minutes. The resulting pH was 9.5. The single handsheets were made at 6.0 pH after adjustment of the pulp suspension with aluminum sulfate solution. The particular starch employed is that marketed by Corn Products Company as Eagle 5071.

(H) The sizing mixture was prepared by the identical procedure as in paragraph G, above, but by substituting another vegetable gum of a non-cationic or non-hydrogen-bonding character for the cornstarch. The pH of the resulting sizing stock was 9.5. Single handsheets were made and coded H. The gum employed was that marketed under the tradename Penford Gum 380 by Penick and Ford Ltd., Inc.

(I) A solution of a cationic material was made up for later use with sizing stock A, above. The solution was made up by mixing 2.5 parts of a cationically modified galactomannan guar gum with 497.5 parts water and then heated to 190° F. The resulting pH was 5.9 and the specific cationically modified gum employed was Draybond II, marketed by Stein, Hall and Company, Inc.

(J) A second solution was made up employing a non-cationic material. The solution was made up to 2% strength by adding 10 parts of an ordinary pearl cornstarch to 490 parts water and heating to 190° F. to attain a final pH of 7.1. The starch employed was Anheuser-Busch A and B pearl starch 7022. This is the same starch as used in sizing stock F, above.

(K) A series of handsheets were made following the procedure set out in paragraph A, above, and further adding 0.25% by weight of the cationic gum solution from I, above, on the basis of the dry fibers. The handsheets were made at pH's of 6.9 and 6.0. These were coded K and K-1.

(L) A series of handsheets were made with the sizing solution of paragraph A, following that procedure, but by following the addition of the sizing stock with 0.25% treatment of the cornstarch solution of paragraph J on the basis of the dry fibers. The handsheets were made at 6.0 pH and coded L.

(M) A sizing mixture was made up by heating 466 parts water and 10 parts cationic white pearl cornstarch to 190° F., followed by adding 20 parts of the fatty acids mixture and 4 parts KOH and boiling for 5 minutes at 210° F. to attain a pH of 9.4. The cationic starch employed is that marketed by National Starch and Chemical Company under the tradename Cato 8. The handsheets were made at two different pH's, these being 6.9 and 6.0, in increasing acidity. The acidity was controlled by the addition of aluminum sulfate solution and thereafter the sizing stock was added. The handsheets were coded M and M-1, respectively.

(N) A sizing stock was made by heating 474.75 parts water and 1.25 parts of a cationically modified galactomannan guar gum and then heating to 190° F., followed by the addition of 20 parts of the fatty acids mixture and 4 parts of KOH and continuing boiling for 5 minutes at 210° F. to attain a final pH of 9.4. The gum employed is that marketed by Stein, Hall and Company, Inc., as Draybond II. Two series of handsheets

TABLE 2

Code No./ Starch or Gum Type	Lbs. Alum/ Lb. Size	Final Forma- tion pH	5 percent NaOH Water Drop (Sec.)	Water Drop Test (Sec.)	25 percent Grain Alcohol Drop Test (Sec.)	Bursting Strength (Mullen)	Internal Bond
Blank..... (Rosin only)	10.8	5.5	24	3,962	410	115	176
A.....	2.4	6.9	12	33	6	110	180
A-1..... (None)	7.2	6.0	1,660	3,669	1,194	106	178
K.....	2.4	6.9	4,504	3,671	49	110	176
K-1..... (Cationic)	7.2	6.0	5,379	4,258	1,542	118	171
B.....	2.4	6.9	2,617	1,502	7	107	166
B-1.....	7.2	6.0	5,268	3,755	1,610	107	170
B-2..... (Cationic)	14.4	5.0	202	4,513	1,739	102	177
N.....	2.4	6.9	2,145	2,858	9	115	160
N-1..... (Cationic)	7.2	6.0	3,814	4,063	1,455	114	158
C.....	2.4	6.9	395	3,313	40	127	175
C-1..... (Cationic)	7.2	6.0	4,016	3,737	1,583	111	173
M.....	2.4	6.9	114	94	6	114	166
M-1..... (Cationic)	7.2	6.0	3,805	3,365	1,285	120	160
D.....	2.4	6.9	354	312	7	105	164
D-1..... (Cationic)	7.2	6.0	3,768	3,668	1,431	118	178
E..... (Non-cationic)	7.2	6.0	548	3,418	719	111	180
F.....	2.4	6.9	10	31	6	119	175
F-1.....	7.2	6.0	205	3,616	583	114	173
F-2..... (Non-cationic)	14.4	5.0	53	3,569	1,661	110	154
G..... (Non-cationic)	7.2	6.0	164	3,769	867	118	167
H..... (Non-cationic)	7.2	6.0	724	3,818	1,062	120	169
L..... (Non-cationic)	7.2	6.0	391	3,758	993	117	167

were made at pH's 6.9 and 6.0, in order of increasing acidity, which was controlled by the addition of aluminum sulfate. The sizing solution was added to the prepared paper pulp at these pH's after the addition of the aluminum sulfate.

Comparison handsheets were made up by employing a fortified rosin sizing. The size treatment was 0.25% based on the weight of the dry fibers. The fortified rosin sizing was first added to the paper pulp, followed by the addition of aluminum sulfate to attain a final pH of 5.5, as is normal in the rosin sizing art. The fortified rosin sizing is that sizing wherein the rosin has been treated with fumaric and maleic acids to attain a modified and improved structure for allowing better water resistance.

The handsheets made according to the above lettered paragraphs on a Noble and Wood handsheet mold were then passed through a wringer and dried on a Noble and Wood drying drum at 40 p.s.i. steam pressure. The handsheets were then conditioned as in the above example at 50% relative humidity at 73° F., for 24 hours prior to the testing. The results of the tests conducted are set out in Table 2, above.

The results of the test conducted on the handsheets set out in Table 2, above, have been arranged for easy comparison of the results of including the cationic materials into the sizing process of the various handsheets. Specifically, code letters A contain no cationic material and show very low sizing properties when 2.4 pounds of alum per pound of sizing acid is employed. However, when a greater amount of alum is employed as in A-1, a more acceptable alkaline resistivity is recorded and other general sizing properties are good. This illustrates the higher alkaline resistivity available as compared to the blank sheet run with fortified rosin sizing, for the saturated fatty acid soaps of the present invention.

The test data in the handsheets wherein a cationic material was employed show that with at least minimum amounts of alum per unit weight of sizing salt, very high values of alkaline resistivity and other sizing properties may be attained. With these cationic materials the alkaline resistivity is approximately 250% as compared when only the potassium salts of the fatty acids are present as in handsheets A and A-1.

The ordinary starches, of a non-cationic character, set out in the lower portion of Table 2, show very low alkaline resistivity, as well as widely varied sizing properties. Hence, it can be said that non-cationic starch and gum materials do not improve the paper sizing in the

manner that the cationic materials do, and that further, they tend to make uniform sizing of papers therewith more difficult than if no starch or gum is employed.

It is also to be noted that there is no significant lowering of the internal bond strength or the Mullen tests with use of the sizing with the cationic materials.

In the following examples, the sizing has been carried out at alkaline pH's and the paper products showed somewhat increased strengths due to the absence of the deteriorating effects of the acidic pH's.

Example III

A series of handsheets were made at 8.0, 7.0 and 6.0 pH and then tested for water and alkaline resistivity.

In order to standardize the test, unbleached kraft pine fibers refined to 520 cc. Canadian Standard Freeness were employed in all of the handsheets. The consistency was 0.53% and the pH 7.7. This slightly alkaline pH was

raised to 9.0 pH by the addition of sodium hydroxide and then further adjusted by either a 0.50% or a 1.0% treatment of calcium chloride CaCl₂. The pulp thus prepared was then given a 0.25% sizing treatment based on the weight of the fatty acids going into the sizing stock and on dry fibers weight. Aluminum sulfate solution was then added to obtain various pH's and the handsheets were made on a Noble and Wood handsheet mold. The aluminum sulfate used was a 3% weight solution of Al₂(SO₄)₃·18H₂O.

The sizing stock was made by first saponifying fatty acids to their respective potassium salts in order to make solution A. 450 parts water, 10 parts KOH and 40 parts of a mixture of saturated fatty acids were heated for 5 minutes at 210° F. Solution B was then made up by adding 5 weight parts of a cationically modified galactomannan guar gum to 495 parts of water and heating to 190° F. The cationic gum employed was that marketed by Stein, Hall and Company, Inc., under the tradename Draybond II. The two solutions were then cooled and sized with the vigorous agitation in order to obtain the sizing stock which had a composition of:

4 weight percent fatty acids } Present as K
1% KOH } salts.
0.5% cationically modified guar gum.

In the sizing stock thus made, the fatty acids analysis was the following—

Acid:	Weight percent
Stearic -----	60.0
Palmitic -----	21.0
Myristic -----	9.0
Oleic -----	5.0
Lauric -----	2.0
Arachidic -----	1.0
Margaric -----	1.5
Pentadecylic -----	0.5
	100.0

A mixture of fatty acids of this composition may be purchased from Amour Industrial Chemical Company under trade name Neofat 18-59, rubber grade. The total unsaturated acid content is 5%, being only oleic acid.

The data obtained from the handsheets sized at various formation pH's which were adjusted with the alum are set out in Table 3, below.

TABLE 3

Percent CaCl ₂ Treatment	Aluminum Ratio, Lbs. Alum/Lb. Size	Formation pH at Time of forming Handsheet	5% NaOH Drop Test, Sec.	Water Drop Test, Sec.	10 minute Immersion Number
0.5-----	2.8	8.0	540	10	984
1.0-----	2.8	8.0	1,200	4,800	294
1.0-----	6.0	7.0	2,340	4,800	360
1.0-----	11.3	6.0	750	10	845

Table 3 shows that the unbleached kraft pine fibers can be sized at from 7.0 to 8.0 pH and still retain high alkaline and water resistivities. This is particularly surprising in view of the deteriorated sizing properties which are obtained by employing a rosin or fortified rosin sizing process at pH's greater than 6.0.

The addition of the water soluble calcium compound was found to provide the effect that high alkaline resistivities could be obtained at final formation pH's higher than 7.0. The amount of the calcium ions present in the solution did not appear critical, but their presence in amounts as shown in Table 3 was found to enable the higher alkaline resistivities to be attained. A theoretical explanation for this effect is not possible at the present time. The primary effect of such calcium ions appears to be that the formation or setting pH may be raised above 7.5 while attaining similar results when no calcium compound is used and the pH is below about 7.5. Also the presence of Ca⁺⁺

in the suspension at pH's under 7.5 has no deleterious effect.

Example IV

A series of handsheet sizing experiments were carried out to show that alkaline and water resistivity may be imparted to a paper sized according to the present invention wherein the sizing reaction is carried out at both high and low final formation pH's. The pH range over which sizing was accomplished in the present example was 5.0 to 11.0. For this example, the potassium salts of the fatty acids, together with a cationic agent, were employed for the sizing stock.

The pulp for this example was unbleached kraft pulp refined by Jordan engines to 58 cc. Canadian Standard Freeness. The stock was prepared by diluting 10 grams fibers to 0.53% consistency and then making handsheets therefrom on a Noble and Wood handsheet mold. The sizing treatment was maintained constant at 0.5 weight percent fatty acids in the sizing stock (present as the potassium salts) based on the weight of the fibers. The aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$ was added in amounts of 1, 4 and 8 pounds per pound of fatty acids with which the sizing stock was made up. Prior to adding the sizing stock to the pulp, sulphuric acid and calcium

of employing the same. The handsheets made therefrom were coded No. 10.

The sizing stock was made up by mixing a mixture of fatty acids having a low unsaturation content with a cationic material in the following manner: 468.5 parts water, 7.5 parts tamarind seed flour, 20 parts of fatty acid and 4 parts of KOH were stirred together at 210° F. for a sufficient time for the saponification of the fatty acids to occur. The gas chromatography analysis of the fatty acids was—

Acid:	Weight percent
Lauric -----	0.5
Myristic -----	6.9
Pentadecylic -----	0.1
Palmitic -----	18.9
Margaric -----	0.5
Stearic -----	73.1
	100.1

The iodine value of this mixture of fatty acids was 1.9 and the acid value 201, while the titer ° C. was 61.5. The degree of unsaturation by weight of fatty acids was 2.0%.

TABLE 4

Handsheet Code	Lbs. Alum Per Lb. Size	pH After Adding Alum	pH Adjusted With H_2SO_4	Final Formation pH Adjusted With $Ca(OH)_2$	5% NaOH Drop Test (Sec.)	Water Drop Test (Sec.)	Liver Blood Test (Hrs.)
1-----	1	6.6	4.0	5.0	352	3,340	+46
	1	6.6	5.0	6.0	1,405	3,142	
	1	6.6	6.0	7.0	2,967	3,368	+46
	1	6.6	None	8.0	1,652	350	
	1	6.6	None	9.0	2,735	391	27
	1	6.6	None	10.0	1,295	213	
	1	6.6	None	11.0	2,676	2,820	+46
4-----	4	5.7	4.0	5.0	1,937	3,393	+46
	4	5.7	5.0	6.0	1,265	3,082	
	4	5.7	None	7.0	2,976	2,977	+46
	4	5.7	None	8.0	2,964	2,748	
	4	5.7	None	9.0	3,240	2,300	+46
	4	5.7	None	10.0	2,740	2,464	
	4	5.7	None	11.0	4,553	5,152	+46
8-----	8	4.8	None	5.0	24	3,685	+46
	8	4.8	None	6.0	850	3,620	
	8	4.8	None	7.0	2,897	3,177	+46
	8	4.8	None	8.0	2,168	1,992	
	8	4.8	None	9.0	3,403	3,214	
	8	4.8	None	10.0	2,832	1,602	
	8	4.8	None	11.0	4,030	5,001	+46
9-----	4	5.7	None	None	120	3,076	29
(Blank)							
(Blank)	8	4.8	None	9.0	11	85	13
			NaOH				
10-----	0	None	9	None	2,246	3,701	21

hydroxide were used to make pH adjustments. The calcium ions were employed in order to widen the pH limits as much as possible. The handsheets formed were made as a series at unit pH's from 5.0 to 11.0.

For the handsheets made, coding numbers were employed to indicate the number of pounds of alum per pound of fatty acids which went into the sizing stock.

As a comparison, a series of handsheets coded No. 9 were made up with a fortified rosin size on a treatment weight of 0.5% which was precipitated with alum at a final formation pH of 5.7. For this blank, handsheets were made at both 4 and 8 pounds alum per pound of fatty acids entering the sizing stock. In the lowest pH sample, No. 9 sized at 8 pounds alum per pound size, an indication of the effect of high pH on a rosin sizing process was attained by raising this pH to 9.0 with calcium hydroxide.

Another comparison handsheet series was made up with a commercially available alkaline resistant size which was employed on a treatment basis of 0.25% size per weight of dry fibers. The pH was adjusted to 9.0 with NaOH prior to sizing. This material attained a high alkaline resistivity as is normal to the product. The main drawback for such materials is the excessively high cost

The sizing data set out in Table 4 shows that when a sufficient excess of aluminum sulfate is employed and calcium ions are present, the unbleached kraft pulp can be sized over a wide range of alkaline pH's to obtain a paper which is alkaline resistant. It is notable that all runs were made with Ca^{++} present thus showing compatibility for this additive over the active pH range. Also, the paper shows generally good sizing properties in that the water drop tests are uniformly high when sufficient alum is employed and the liver blood test shows extremely good resistance to such materials, identifying an extremely effective sizing process for the production of butcher's wrap. Run Series 1 shows that 1 lb. alum per pound fatty acids is on the border of the necessary ratio. The water resistance is low for pH's 8.0-10.0.

As in the above examples, the sizing process set out herein allows a total range of valuable sizing properties to be established in the sized product. One of these properties is that the alkaline resistivity is uniformly high from 7.0 pH (neutrality) to 11.0 pH. An alum precipitation sizing process operating in this alkaline range has not been heretofore disclosed. Another of these properties is shown by the extremely high values of the liver blood tests, along with high values for water resistance. In order

to produce a sized fiber product which retains all of the sizing properties except the alkaline resistivity, the guidelines of the present example may be followed with the exception that the concentration of the insoluble soap size

sheet was made by adjusting the pH of the 0.53% consistency fibers suspension to 9.0 pH with NaOH followed by the addition of the size at 0.25% treatment. The hand-sheet was coded 15.

TABLE 5

Hand-sheet Code	Lbs. Alum Per Lb. Size	pH After Adding Alum	pH Adjust-ments with H ₂ SO ₄	pH Adjust-ments with Ca(OH) ₂	Photo-volt Bright-ness	5% NaOH Drop Test (Sec.)	Water Drop Test (Sec.)	Liver Blood Test (Hrs.)
Blank	0	7.0	7.0	7.4	77.0	9	7	-----
1	1	6.2	4.0	5.0	77.0	2,425	4,469	-----
2	1	6.2	5.0	6.0	78.0	3,939	5,425	+46
3	1	6.2	6.0	7.0	78.0	3,666	4,400	-----
4	1	6.2	None	8.0	76.5	1,447	25	-----
5	4	4.5	4.0	5.0	79.0	3,842	5,266	-----
6	4	4.5	None	6.0	78.0	4,326	4,515	+46
7	4	4.5	None	7.0	79.0	4,376	3,781	-----
8	4	4.5	None	8.0	78.5	4,336	43	-----
9	8	4.0	None	5.0	80.0	3,534	4,481	-----
10	8	4.0	None	6.0	78.5	4,158	3,796	+46
11	8	4.0	None	7.0	79.0	2,292	25	-----
12	8	4.0	None	8.0	78.0	2,794	48	-----
13	8	4.0	None	9.0	78.0	7	7	-----
14	4	4.5	None	4.5	78.0	51	4,674	27½
NaOH								
15	0	None	None	9.0	77.0	2,194	3,915	46

in the fiber product can be decreased to a desired level, usually about 2 lbs. (measured on the weight of the fatty acids) per ton of dry fibers. Such a sized fiber product then offers an alternative to the use of the widely employed rosin and fortified rosin sizings.

By comparison, the handsheets sized with a 0.5% treatment of fortified rosin size gave practically no alkaline resistance at either of the two widely spaced alum amounts used. As expected, the expensive alkaline resistance sizing showed generally good alkaline and water resistivity.

Example V

A series of handsheets were made employing a bleached kraft pulp to determine the effect of the size of the present invention upon the brightness of the product and to evaluate the bleached pulp product. The pH range employed was from 5.0 to 8.0. Other test evaluations were for alkaline resistivity, water resistivity and liver blood holdout.

The sizing stock of Example IV was employed. Bleached kraft pine pulp refined to 550 cc. Canadian Standard Freeness was diluted to 0.53% consistency and exhibited a pH of 7.0. Handsheets were made from 10 gram samples of the fibers with a 0.5% treatment of a size based on the weight of the fatty acids entering the sizing stock to a basis weight of the fibers. A first series of the handsheets was made at one pound alum per pound fatty acids and the sizing stock and numbered 1-4. A second series was employed at four pounds alum per fatty acids and numbered 5-8, while a third series was made employing eight pounds alum per pound fatty acids and numbered 9-12. In each of the series of handsheets employed, pH adjustments were made where necessary in order to attain an acid pH or an alkaline pH by addition of either sulphuric acid or calcium hydroxide. Thus, after the addition of the alum, acid pH's were maintained in most instances which only necessitated the addition of calcium hydroxide, while in those pulp suspensions wherein a lower pH was desired, the adjustments were made with sulphuric acid.

A comparison sheet was made up with a fortified rosin size on the basis of 0.5% treatment for the fibers after which alum was added at a final formation pH of 4.5. A second handsheet was sized after adjustment with calcium hydroxide to attain a pH of 9.0. These sheets were coded 13 and 14. In order to show the effect of these various sizing products with respect to a blank (blotter sheet formed with no sizing), a run was made and is set out at the top line of Table 5, below.

Another comparison handsheet made up was that with a commercially available alkaline resistant size. The hand-

The test data obtained and set out in Table 5, above, illustrates that the bleached kraft pine pulp may be employed to make a paper product in which the brightness is not diminished by the presence of the polyvalent metal soap sizing. While the brightness range was tested over a pH range of from 5.0, acid, to 8.0, alkaline, it is believed that extending the range upwardly in Example IV would not diminish the brightness of the paper product. Also, higher amounts of the alkaline resistance size may be employed in the pulp to attain yet higher alkaline resistivities without diminishing the brightness.

A treatment of 0.5% fortified rosin size at 4.5 pH gives practically no alkaline resistivity but excellent water resistance as is normal, while the higher, alkaline pH sizing of the fortified rosin gave no sizing properties. As expected, the expensive alkaline resistance sizing, which requires no alum for precipitation, showed high values for sizing properties.

Example VI

To illustrate a commercial employment of the present invention, a run of 2463 tons of a kraft paper liner was made on a Fourdrinier paperboard machine. The duration of the run was 88 hours.

The run was made with unbleached kraft pulp produced by cooking pinewood pulp according to the kraft pulping process. The pulp was then refined to the freeness desired for the primary and for the secondary stock and then introduced into the paperboard machine by the appropriate fan pumps. The Fourdrinier machine employed had the usual two stock systems in which the primary stock, the base sheet, was laid down followed by the laying of the top liner stock, the secondary stock thereupon and pressing and drying to a final paper product. This is the normally employed kraft paper producing process.

The primary stock was refined to an average Canadian Standard Freeness of 640 cc. and treated with 21.3 pounds of alum per ton of primary stock. The alum employed was that known as papermakers' alum. After the addition of the alum, 2.4 pounds of sulphuric acid per ton of pulp was added for pH lowering. The prepared size was added at the primary fan pump at the rate of 4.5 pounds of fatty acids per ton of dry pulp.

The secondary stock, the top liner, was refined to an average Canadian Standard Freeness of 310 cc. Sulphuric acid was then added for pH control after refining; the alum was added at the secondary fan pump at the rate of 18.9 pounds per ton of secondary stock. The prepared sizing solution was also added at the secondary fan pump at the rate of 3.75 pounds per ton of secondary stock.

The primary stock was maintained at a 0.54% consistency and 130° F. while the pH was controlled to 7.1. The secondary stock was maintained at 0.75% consistency and 130° F. while the pH was controlled to 7.1 pH, also.

The primary and secondary stocks then flowed as aqueous dispersions onto the Fourdrinier wire forming element. The alum reacted with the potassium salts of the fatty acids in the presence of the cationic material to precipitate the fatty acid salts in a dispersed manner so that upon draining of the pulp on the forming wire, the sizing was uniformly distributed throughout the paper web. That is, the size is not concentrated on one surface of either the primary or secondary stock or layers. After laying out on the wire, the paper was run over the conventional drying rolls of the paper machine at normal temperatures of 200–230° F. to expel the water and then taken up in rolled form.

In this commercial run, the sizing stock contained 4% by weight saturated fatty acids, 1.5 weight percent tamarind seed flour which is a naturally occurring hydrogen-bonding gum, and excess KOH in amount of 0.8 weight percent. The sizing stock contained the fatty acids in the form of their potassium salts and was maintained at 110–140° F. prior to mixing into the secondary fan pump.

The sizing stock was made up by heating 300 pounds of the tamarind seed flour and 160 pounds of the potassium hydroxide to 180° F. in 1600 gallons of water followed by the addition of 800 pounds of the fatty acids. This mixture was then heated to 190° F. and made up to a final volume of 2400 gallons at 190° F. This process resulted in the formation of a sizing stock having the above amount of ingredients therein.

An analysis of the fatty acids employed was—

Acid:	Percent by weight
Caprylic -----	0.17
Capric -----	0.35
Lauric -----	0.85
Myristic -----	2.72
Pentadecanoic -----	0.85
Palmitic -----	41.26
Margaric -----	2.38
Stearic -----	45.84
Oleic -----	5.60

A fatty acid mixture of the above composition may be obtained from Darling Chemical Company under the trade name DAR S-77.

For the sizing stock, the tamarind seed flour may be obtained from Dycol Chemicals, Inc. under trade name Dycol D-16.

As the run was conducted, samples were taken at regular intervals and conditioned 24 hours at 50% relative humidity at 73° F. prior to testing. The average of 10 tests taken throughout the run is set out in Table 6, below.

Average tests of ten rolls of paperboard	
Weight (lbs./1000 square ft.) -----	46.5
Caliper in inches -----	.013
Mullen -----	132
Conditioned Moisture -----percent--	7.0
Internal Bond -----	106
Tear: Md -----	330
Elmendorf Cd -----	403
Photovolt Brightness:	
Top Side -----	19.2
Bottom Side -----	19.1
5% NaOH drop test:	
Top Side -----minutes--	37½
Bottom Side -----do-----	27
Alcohol drop test:	
(25% Grain)	
Top Side -----do-----	24
Bottom Side -----do-----	18¾

Average tests of ten rolls of paperboard

Water drop test:	
Top Side -----do-----	+60
Bottom Side -----do-----	+60
Cobb water size test:	
(Grams/Sq. Meter)	
Top Side -----	37
Bottom Side -----	34
10 Minute Immersion No. -----	421

The Mullen is a standard strength test in a Mullen tester and shows an equivalent average value to the sizing of kraft pulp by rosin.

The alkaline resistivity as recorded by the NaOH drop tests and the alcohol resistivity as recorded by the alcohol drop tests, together with the water drop tests, are recorded in minutes due to the long times of holdout against such substances. These values are all high, both for the top side, secondary layer and the bottom side, the primary layer.

This example is particularly valuable for illustrating the amounts of the fatty acids which may be commercially employed for unit weight of the dry pulp. The primary stock was sized with 4.5 pounds of the fatty acids going into the sizing stock per ton of dry pulp. This amounts to 0.225 weight percent sizing based on the dry pulp weight. The secondary stock was sized with 0.1875 weight percent sizing treatment. At these sizing percentages of from 0.1 to 0.3, the sizing process of the present invention may be carried out economically with respect to the competitive rosin sizing processes. Hence, a new sizing process and products have been herein set out which allow the attainment of greatly improved sizing properties while remaining low enough in cost, in the present market, to offer an alternative to the employment of rosin sizing.

Proportions

As little as 0.05 weight percent of the fatty acids in the sizing stock may be employed on the basis of the dry fibers to get low sized fiber products. Such a weight is one pound per ton of the dry fibers. Alternatively, for other products, as high as ten weight percent may be employed to get 200 pounds per ton of dry fibers. At sizing amounts over this upper limit, the amount of fibers is so low as to adversely affect the paper strength. For special employments, this may be increased, as there is no critical upper limit.

Generally, 3.0 pounds size (measured as fatty acids) per ton of the dry fibers may be employed to get approximately a 25-minute secondary stock alkaline measure. For the primary stock, a higher sizing amount of 7.0 pounds per ton is needed on unbleached kraft to get a similar alkaline holdout. Depending upon the particular employment for the paper product, sizing from three pounds per ton to seven pounds per ton is the most economically feasible. With such limits, significant alkaline resistivity may be established, together with good water and alcohol resistance.

In summary, a sizing at 2.0 pounds of fatty acids per ton of dry pulp will allow the total sizing properties of the rosin sized paper products to be attained. For high alkaline resistivity a higher amount of 7.0 pounds fatty acids per ton of dry pulp is usually necessary. Hence, while the sizing stock of the present invention may be employed to attain high alkaline resistivities, it also may be employed to produce a paper having equivalent water resistance property to the ordinarily employed rosin sized products. At the same time, higher sizing concentration of from 7.0 to 20 pounds per ton fibers may be employed to manufacture such materials as wallboard covers for gypsum wallboard. Increasing the sizing concentration does not deteriorate the high alkaline resistivity and therewith insoluble size concentration meas-

ured as fatty acids weight may be from 0.15 percent to 4 percent for most products.

Other uses are evident from the good water holdout which indicates a good ink holdout, as well as the liver blood tests which illustrate particular packaging uses.

Proportion ranges within which the sizing process should be carried out are the following: The pulp consistency can be from approximately 0.2% to 5% of dry fibers to the total pulp stock weight. The consistency of the pulp stock is not considered critical and may be employed over wide ranges as desired. As stated above, the pH range can be from as low as 5 to as high as 11.0.

The cationic material employed according to the present invention may be present over the range of from 0.1 to 5.0 weight parts per weight part of the fatty acids entering the sizing stock, and present therein as the alkaline metal or ammonium salts of the acids. For precipitation of the salts of the fatty acids, the water soluble precipitating agent for releasing the polyvalent metal ions may be used in an amount of from 1.0 to 12.0 weight parts per weight part of the entering fatty acid salts. This range extends over this stoichiometric amount necessary for a metathesis reaction of exact proportions.

For the sizing stock the fatty acid salts may be present therein in an amount of from 0.2 to 30 weight parts per 100 parts of sizing stock. As above, the cationic material may be present in an amount of from 0.1 to 5 weight parts per weight part of the fatty acid salt (measured as fatty acids entering the sizing stock). The remainder of the sizing stock is free alkali and water.

The proportions of the components of the sized fiber products are those set out above for the sizing process. The combination of ingredients employed in this sizing process allows an almost complete pickup by the fibers of the sizing constituents, resulting in an extremely economic sizing.

Uses of the sized fiber products produced by the present invention are the production of butchers' wraps, soap wrappers, soap containers, cement bags, lime bags, paper materials used in the manufacture of sheet rock building modules, paper containing calcium carbonate as a filler, gum tapes, printing papers, billboard papers, offset paper, gravure papers, as well as many of the kraft paper grades of products.

From the above examples, it can be seen that the sizing process of the present invention may be carried out over a wide pH range of from 5.0 to 11.0 to attain uniformly high sizing properties over an entire range. The most efficient method of expanding the available pH range is with a pH adjustment to the higher pH's of an alkaline material which releases calcium ions. The normal of these are calcium chloride and calcium hydroxide. However, for performing the sizing process, the use of the calcium ions is not required as is seen in Example VI, which illustrates a commercial run, and in Examples I and II.

Particularly, once a given pH range is established for commercial production, and this pH is close to neutrality or slightly acidic, an additional treatment with a calcium ion liberating material is not required.

The 30% upper limit for the unsaturation content of the fatty acids employed in accordance with the present invention has been established by the previously known sizing processes employing such fatty acids. Further, the preferred upper limit of 7% has been determined to consistently produce the high alkaline resistivity desired in the products having that property made by the present invention.

It can be seen from the statements made herein that the cationic material to be employed with the salts of the fatty acids can be any of the material classified as cationically active starches, cationically active gums, hydrogen-bonding starches, and hydrogen-bonding gums, providing that they are all water soluble over temperatures of from about 100 to 150° F.

It is obvious that the specific examples are not restrictive, and that the invention may be practiced in other ways within the scope of the appended claims.

I claim:

1. The method of making a sized fiber article having high resistance to alkaline environments which comprises the steps of mixing cellulose fibers and aqueous suspension maintained at an elevated temperature with a homogenous mixture of substantially saturated fatty acid salts having a cation selected from the group consisting of sodium, potassium, and ammonium ions, the fatty acid radicals thereof having from 12 to 20 carbon atoms and a material selected from the group consisting of cationically active starches, cationically active gums, hydrogen-bonding starches, and hydrogen-bonding gums, said mixture having said material present in the amount of from 0.1 to 5.0 weight parts per weight part of the fatty acids of said salt, and with a water soluble precipitating agent for provoking the forming of water insoluble soap throughout the fiber mass, said precipitating agent providing ions selected from the group consisting of aluminum, ferric, and chromic ions, and thereafter separating water and soluble wastes from the fiber mass and the insoluble soap sizing and therewith forming said article.

2. The method of claim 1 wherein said mixing step is conducted within a pH range for the aqueous suspension of from 5.0 to 7.5.

3. The method of claim 1 wherein said mixing step is conducted with fatty acid salts in amounts such that the ratio of the weight parts of the fatty acids of said salts to the weight parts of dry fibers is within the limits of 0.05:100 to 10:100.

4. The method of claim 1 wherein said mixing step is conducted with the weight ratio of the precipitating agent to the fatty acid salt within the range of 1:1 to 12:1.

5. The method of claim 1 wherein the cellulose fibers are diluted with water to a consistency of from 0.2 to 5.0 weight percent fibers before the mixing step.

6. The method of claim 1 wherein said mixing step is conducted with a pH range which is adjusted by the addition of a compound selected from the group consisting of alum, sulfuric acid, and alkaline metal water-soluble compounds.

7. The method of claim 1 wherein said mixing step is conducted within a pH range for the aqueous suspension of from 7.5 to 11 with a water-soluble calcium compound.

8. The method of making a sized fiber article having high resistance to chemicals, including alkaline substances, which comprises the steps of diluting cellulose fibers with water to a consistency between the limits of 0.2 to 5.0 weight percent fibers, adjusting the pH of the aqueous suspension of fibers to from 7.5 to 11.0 by addition of from 0.5 to 2.0 weight percent of a water-soluble calcium compound based on the weight of the dry fibers, maintaining the temperature of the aqueous suspension in the range of about 90° F. to not greater than 135° F., mixing therewith a homogenous mixture of fatty acid salts and a material selected from the group consisting of cationically active starches, cationically active gums, hydrogen-bonding starches, and hydrogen-bonding gums, the ratio of the weight parts of the fatty acids of said salts to the weight parts of dried fibers being within the limits of 0.05:100 to 10:100, said material present in an amount of from 0.1 to 5.0 weight parts per weight part of the fatty acids of said salts, and with a water-soluble precipitating agent for provoking the formation of water-insoluble soap throughout the fiber mass, said precipitating agent providing ions selected from the group consisting of aluminum, ferric, and chromic ions, said fatty acid salts having a cation selected from the group consisting of sodium, potassium, and ammonium ions, the fatty acid radicals thereof having from 12 to 20 carbon atoms and said salts having less than 30 weight percent unsaturated fatty acid radicals, and thereafter separating water and

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soluble wastes from the fiber mass and the insoluble soap
sizing and therewith forming an article.

References Cited

UNITED STATES PATENTS

1,840,399	1/1932	Lane	162—179	X
1,884,563	10/1932	Carson	162—175	X
2,056,209	10/1936	Rafton	162—179	X
2,124,372	7/1938	Kesler	162—175	X

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2,195,600	4/1940	Reilly	162—178	X
2,250,115	7/1941	Mayer et al.	106—206	
2,935,436	5/1960	Caldwell et al.	162—175	
3,017,294	1/1962	Meisel	162—175	X
3,223,543	12/1965	Savina	162—175	X

FOREIGN PATENTS

12,769	1901	Great Britain.
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