Sept. 6, 1966 W. J. KARI ETAL 3,271,240
PROCESS OF SIZING WATER-LAID SHEETS
WITH A CATIONIC ASPHALT EMULSION
Filed Nov. 20, 1962 4 Sheets-Sheet 1

CATIONIC SIZE SIZES BEST WITHOUT FLOCCULENT

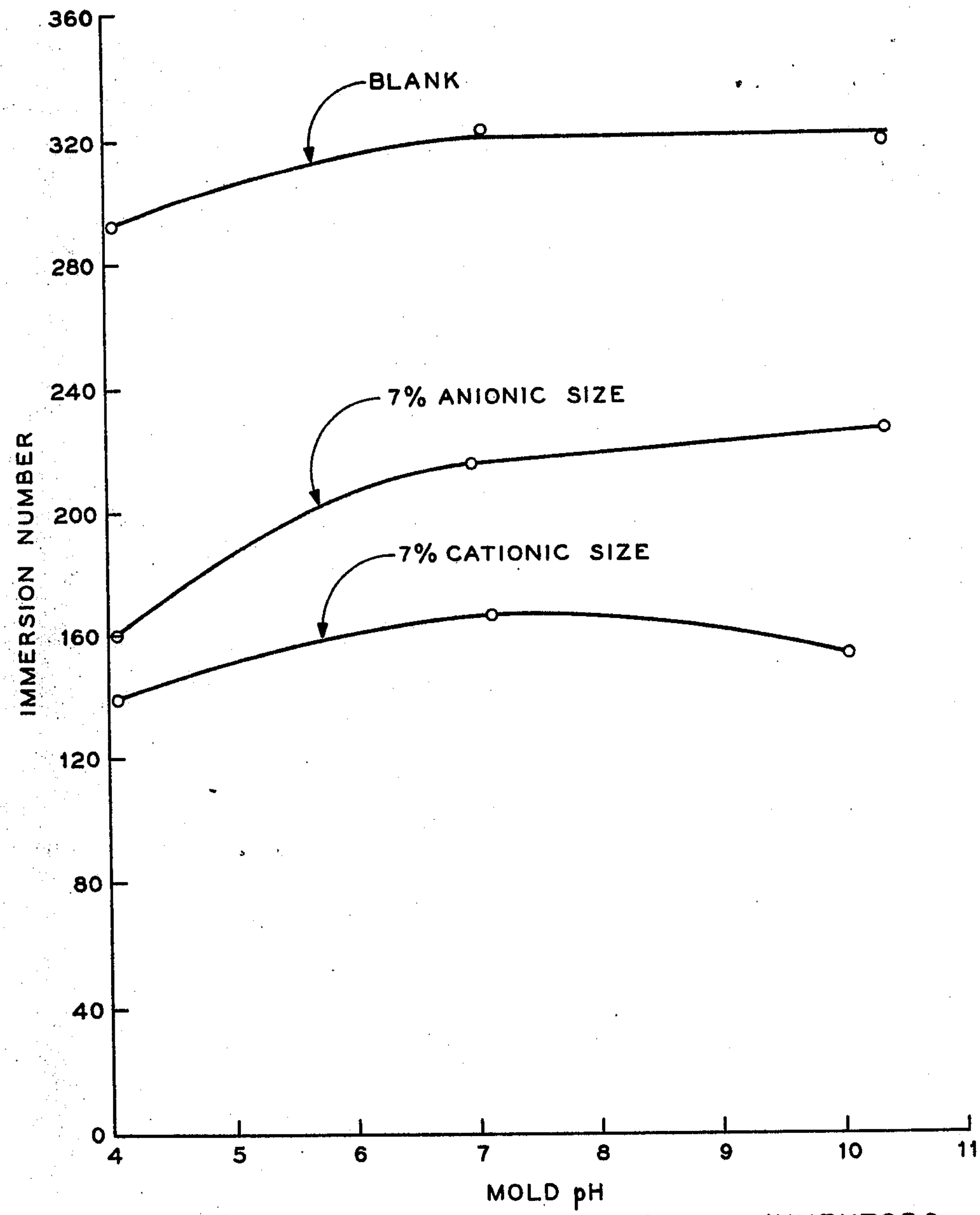

FIG. 1

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CATIONIC SIZE GIVES BEST WET STRENGTH WITHOUT FLOCCULENT

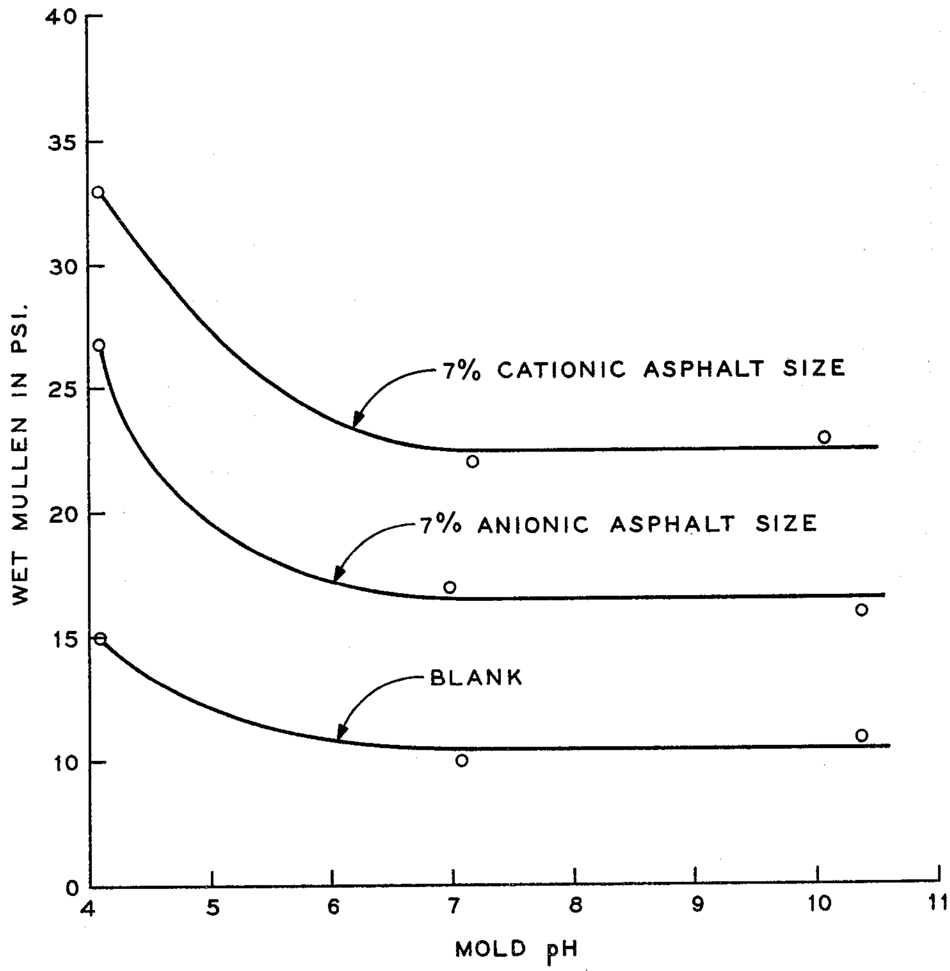

FIG. 2

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Sept. 6, 1966 W. J. KARI ETAL 3,271,240
PROCESS OF SIZING WATER-LAID SHEETS
WITH A CATIONIC ASPHALT EMULSION
Filed Nov. 20, 1962 4 Sheets-Sheet 3

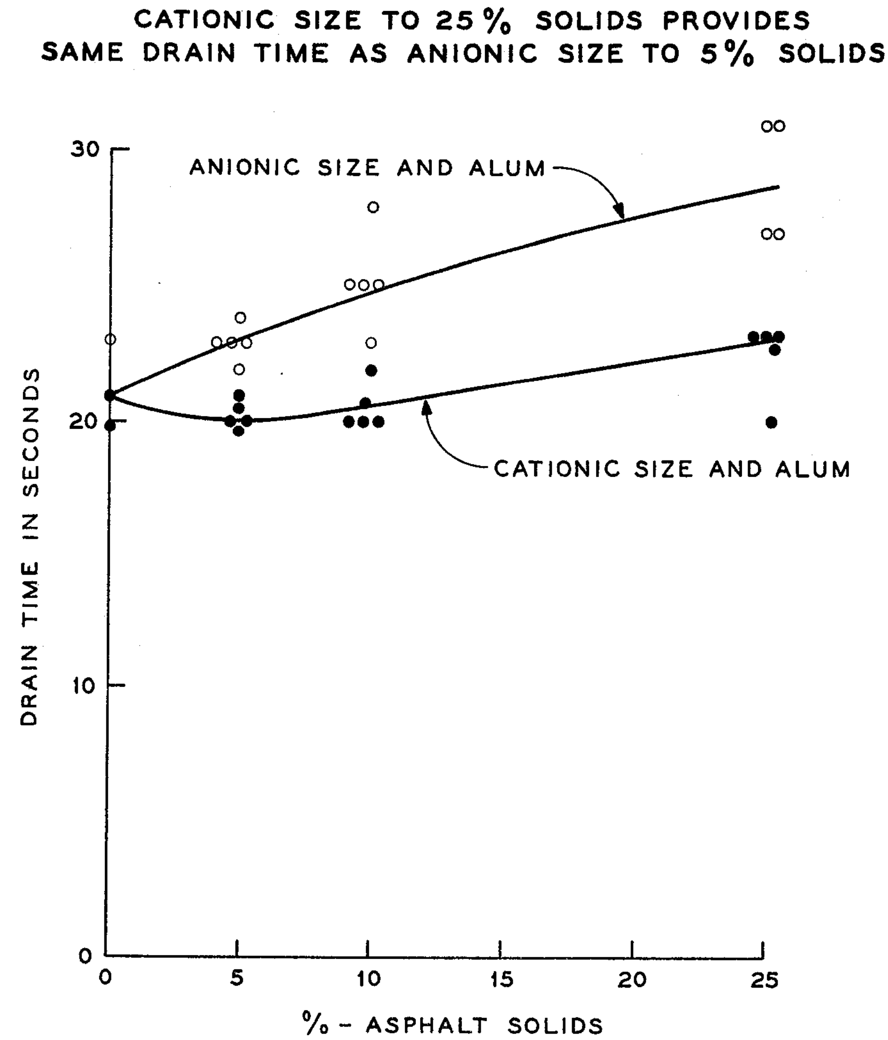

FIG. 3

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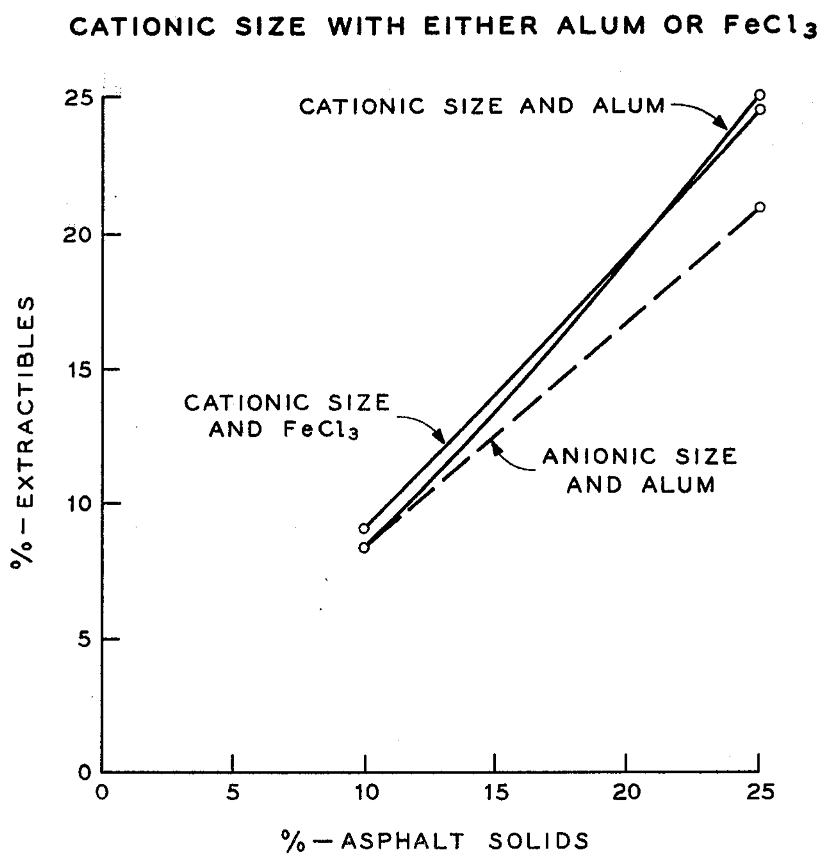

FIG. 4

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PROCESS OF SIZING WATER-LAID SHEETS WITH A CATIONIC ASPHALT EMULSION

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7 Claims. (Cl. 162—171)

The present invention relates to an improvement in the manufacture of paper, paperboard (including corrugated boxboard and laminated fiberboard), structural board, and the like. In particular, the invention concerns production of improved paper, paperboard, structural board and the like products rendered water-resistant by "sizing" the wet fibers with bituminous materials introduced into the cellulose pulp stock in the form of a cationic emulsion of a bitumen in water. The paper and board thus produced are high strength materials owing to the presence of a larger proportion of bituminous size than heretofore was considered possible for the manufacture of paper and board of satisfactory quality. Furthermore, the application of the cationic bituminous size unexpectedly improves the drainage of water from the pulpstock webs on the wires of the forming machinery and results in a faster and better formation.

The terms "paper and paperboard" as employed herein refer to sheets prepared from vegetable cellulose fibers with the lignin almost completely removed therefrom by one of the known chemical treatments of the pulp. The term "structural board," on the other hand, refers to a coarse fibrous board prepared from the mechanically defibrated wood or plant fiber pulp which retained its lignin content.

Introduction of solid comminuted bitumens, such as asphalt, for the purpose of sizing pulp stocks in lieu of the previously employed "rosin," is well known in the art; see, for instance, U.S. Patent No. 1,288,158, issued to Perry in the late twenties.

Because of the difficulties encountered in incorporating solid comminuted bitumen in aqueous pulp in the actual commercial practice, it has been later suggested to introduce the bituminous size in the form of a clay-type emulsion. This procedure is described in a number of patents issued to Kirschbraun, for instance, in U.S. Patents Nos. 1,615,303 and 1,722,434. However, despite the initial success of the clay emulsion-type size, certain difficulties hampered its acceptance by the industry. It was noted that, at the high dilutions of the fiber stocks commonly used for making paper and board (0.1 to 0.3% fibrous solids in the manufacture of paper and 1 to 3% in the production of structural board), the comparatively large size of the clay emulsion particles ranging from 5 to 40 microns in diameter apparently hinders sizing efficiency and tends to interfere with the smooth and economical formation of satisfactory strong paper and board.

Then it has been proposed to add the bituminous size to pulp stocks in the form of anionic emulsions of bitumen in water. This development, which dates from the time of World War II and is illustrated by the disclosures of U.S. Patent 2,481,374, issued to Watts and Thompson, made possible production of a more satisfactory product than has been manufactured heretofore with other conventional size materials, such as rosin and wax. This technique permitted introducing into the product as much as 10 and up to 15% by weight of bitumen (such as asphalt), based on dry fiber. However, here again, certain drawbacks in the use of anionic emulsions of bitumen, and, specifically, of asphalt, soon became apparent.

First of all, there was the maximum limit of bituminous size of about 10, at most 15% by weight, based on dry fiber weight, which could not be exceeded when resorting to anionic bituminous emulsions, lest the speed of the machinery, and specifically the rate of travel of cylinder molds and Fourdrinier wires, be considerably slowed down.

Secondly, the actual fixation of bitumen (asphalt) size from anionic emulsions thereof with alum, or other like flocculents, on the fibers is not an entirely chemical mechanism, so that at first some of the particles of bitumen precipitated by alum become mechanically entrapped thereby in the pulp, but eventually some of the bituminous size does filter out during the formation of the sized pulp on the wires. This lack of retention of the size accounts for the dark color of the drain water—an objectionable feature—and results in a loss of the size.

Moreover, one is limited by the fact that, contrary to some wishful statements in the art, the flocculent (setting agent) is not fully effective, unless added to the pulp before the addition of the "anionic" size. It has been suggested by some of the proposed techniques that anionic asphalt emulsions can be used to size pulp stocks having a pH on either the acid or the alkaline side by treating the pulp stock accordingly with an alkaline or an acid material prior to the application of the anionic asphaltic size. Accordingly, small amounts of alum, for instance, have been added to the pulp to adjust its pH; however, in the absence of such adjustment and using alum only as a flocculent, it has been noted that the application of "anionic" bituminous size is not satisfactory unless the size and the flocculent are added to the pulp in the last stage before it arrives on the wires, namely, into the head box (last machine chest). This, however, more often than not leaves insufficient time for contact, with consequent failure of the alum to assist effectively in precipitating the size on the fibers, and results in a further darkening of the drained water, and in a loss of the bituminous (asphalt) binder.

Another drawback is the undue retention of water in the pulp mix, apparently resulting from the tendency of the sized and alum-treated pulp stock to retain the water owing to the formation and presence of a metallic soap complex. In addition, this soap entraps air and causes foaming, and the foam hinders the drainage of water.

In the more recent years, cationic asphalt emulsions made their appearance in the field of paving construction and repair and rapidly gained recognition as a paving material competitive, and, in many instances, superior to the previously employed anionic emulsions. These cationic asphalt paving emulsions are characterized by a high asphalt residue content from about 50 to 75%. While the applicability of cationic emulsions of asphalt became recognized in the paving industry, the paper and board industry, where anionic asphalt emulsions were used competitively to the rosin size, failed to explore the possibilities offered by the cationic asphalt emulsions and other kindred bituminous emulsions for internal sizing of paper pulp.

What could have been the actual reasons is hard to guess: it may have been the result of a reluctance to pay considerably higher prices commanded at first by cationic emulsifiers for asphalt size emulsions as compared with the cost of the already publicized and tested anionic asphalt emulsions suitable for paper sizing, or yet, perhaps, it was a simple failure by the paper and board industry to consider the possibility that these cationic emulsions, if and when employed for sizing the pulp, might bring about considerable and unexpected improvements in the manufacture and in the quality of the final product. The fact remains, however, that the industry has not heretofore applied the cationic emulsified asphalt for sizing operations, did not investigate the effect of such sizing on the operation of the paper and board manufacturing processes, and did not investigate the effect of such sizing on the various properties desirable in paper and board. In all events, it never made public the results of such investigations or indicated heretofore that it planned to do so.

Besides, at a first, initial comparison, if one were contemplating the use of cationic asphalt emulsion for internal sizing of paper pulp, the ultimate product fabricated from the pulp stock sized with cationic asphalt would not seem to be different from the product obtainable from the pulp sized with anionic asphalt, whether in the absence or presence of a flocculent, such as alum. Both will be made up of the same cellulose fibers sized with asphalt solids.

However, it is now found that apparently due to the different nature of the electrical system available in cationic emulsions, as contrasted with anionic emulsions, application of cationic bituminous emulsions for sizing the pulp in the production of paper, paperboard and structural (insulating) board brings about unexpected improvements, both as regards the very operation of the manufacturing process and as regards the quality of the paper and board thereby produced.

Emulsions which in accordance with the present invention may be employed for sizing the pulp in the manufacture of paper and board are prepared by emulsifying bitumen, such as asphalt, in water with the aid of oil-soluble, cationic, basic nitrogen-containing emulsifiers found in the group consisting of amine salts and salts of quaternary nitrogen bases. Any of these basic nitrogen-containing, oil-soluble, cation-active salts in sufficient amounts to produce emulsions of bitumen in water, characterized by a bitumen residue of from about 50 to as high as 80% by weight, and preferably from about 55 to about 70% by weight, may be employed as cationic emulsifiers. Provided necessary cooling is applied directly after the emulsification of bitumen to assure emulsion stability, the resulting emulsions will be effective as sizes for the cellulosic fibers of the pulp, whether applied with or without formerly required flocculents, such as alum.

Pulps sized with cationic bituminous emulsions according to the invention can be effectively processed to the desired paper or board products at a pH of the sized stock mix in the range from about 3.5 to about 10.0. If, in operating with a pulp having an acid pH, an acidic flocculent is furthermore employed, the pH may be even lower than 3.5. With alum, which apparently has a buffering action, the pH usually is not lower than 4.0. Pulps with an alkaline pH may be also effectively processed by suitable additions of alum or the like materials.

It has been found that oil-soluble, cation-active salts of alkylene diamines having the general formula $RNHR'NH_2$ are particularly effective and advantageous. In the formula of these diamines, R is an acyclic hydrocarbon group of from about 8 to about 20 carbon atoms and R′ is an alkylene group containing from 2 to 3 carbon atoms. Preferably the acyclic hydrocarbon group of the diamine contains from about 12 to about 18 carbon atoms, as in the alkylene diamine material, particularly effective for the preparation of bituminous size, and sold in the trade under the registered trademark "Duomeen T." In this particular diamine material, R is formed by acyclic (mainly C_{16}–C_{18}) hydrocarbon groups derived from tallow fatty acids and R′ is a propylene group.

Other alkylene diamines in which R is an acyclic hydrocarbon group derived from oleic acid, coconut oil fatty acids, tall oil acids, corn oil fatty acids, olive oil fatty acids, palm oil fatty acids or the like also may provide salts effective as cationic emulsifiers for bituminous sizes for use in the paper and board industry in accordance with the present invention.

Any acid that will form an oil-soluble salt emulsifier without causing precipitation of the salt will be suitable to furnish the anionic portion of the cation-active emulsifier. Thus, sulfuric acid which is apt to cause precipitation is unsuitable to form the anion. On the other hand, the anion portion of these salt emulsifiers may suitably be either a halide, a nitrate, an acetate, a tannate, a phosphate or a citrate; chlorides of alkylene diamines described hereinabove are presently preferred for the preparation of cationic bituminous (asphalt) sizes. The pH of these cationic emulsions, upon preparation, may range from about 1.5 to 3.0.

As pointed out hereinbefore, cationic bituminous emulsions of the invention effectively size the pulp stocks in the manufacture of paper and board (both paperboard and structural board), as it is shown by the data presented further on in this description, and will contribute to the formation of superior products.

However, whenever desired, and particularly in order to reduce water pick-up, flocculents may be used, alum being the one preferred.

When the cationic bituminous emulsions formed with the aforementioned salts as emulsifiers are used to size the pulp in conjunction with a flocculent, such as alum or ferric chloride, the resulting complex formed by (1) the pulp fibers, (2) the cationic bituminous size emulsion and (3) the flocculent, does not hold water as strongly as the like complex obtained in using the anionic bituminous emulsion size. The positively charged particles of bitumen in the cationic emulsion thereof, owing to their electrical affinity to the negatively charged cellulosic pulp fibers, deposit themselves on the fibers irrespective of the presence of alum or the like; and, although a flocculent such as alum, may be added to provide a further reduction of the tendency to pick up water and a great strength, less flocculent will be necessary than in thecase of an anionic bituminous size. Considering the tremendous quantities of flocculents, and particularly of alum, consumed by the industry, this represents a significant improvement. Moreover, the drainage and drying of the pulp mix formation on the wires, or on the dryer drums, also requires less time.

When employing the aforementioned preferred alkylene diamines to produce salts for use as cationic emulsifiers in preparing the bituminous size for the manufacture of paper and board, from about 0.25 to about 2.50%, preferably from about 0.75 to about 1.75%, by weight of a suitable alkylene diamine, such as "Duomeen T," based on the final emulsion, will be found effective for emulsifying a bitumen, such as asphalt, in amounts from about 50 to about 80%, and preferably from about 55 to about 70% by weight, the balance to 100% being water.

The actual emulsification of bitumen is carried out readily in a conventional manner, by dissolving the alkylene diamine in water at about 160–180° F. and then adjusting the pH of the solution and converting the diamine to a salt by a suitable addition of acid, equal to or preferably slightly in excess over the quantity of the diamine. Thus, when a chloride salt is to be used as the cationic emulsifier in the preferred range of amounts from 0.75 to 1.75% by weight as mentioned hereinbefore, hydrochloric acid is added in an amount slightly in excess (for instance, 0.25%) over the quantity of the diamine. Thereafter hot bitumen, e.g., asphalt is dispersed in this aqueous solution in a suitable apparatus, for instance, in a colloid mill, and an emulsion of bitumen is recovered at the discharge outlet of the mill, the particles of bitumen in this emulsion being 5 or less, preferably 1 to 3 microns in size.

The viscosity of the cationic bituminous emulsions suitable for sizing the pulp in accordance with the invention is not a critical factor, so long as it is sufficiently fluid to be dispersible in the pulp stock; for all practical purposes, viscosities from abount 15 to 100 SSF at 77° F. are satisfactory. Preferably the emulsions should not be subject to undue settlement likely to impair their usefulness for sizing fibers.

Among suitable bituminous materials for the preparation of cationic emulsion size, asphalts characterized by penetration values in the range from 0 to about 30 at 77° F. (ASTM D5–52) and by softening points in the range from about 160 to about 260° F. (ASTM D36–26, Ring and Ball Method), may be used. Preferably the asphalts will have a softening point from about 180 to about 230° F. and a penetration from 0 to about 15.

Suitable bitumens include all kinds of asphalts, capable of emulsification when heated to from about 300 to about 450° F. irrespective of the manner of their production, namely, steam-refined, solvent-refined and air-blown asphalts.

High melting coal-tar pitches, such as are recovered in the coal-tar production from horizontal coke ovens, gaswork retorts, blast furnaces and the like, having substantially similar penetrations and softening points and similar viscosities which permit emulsification if and when heated to 300–450° F., as the aforementioned asphalts, also may be emulsified to form stable cationic bituminous emulsions for use as sizes in accordance with the invention.

Among other bituminous materials, the so-called "native" asphalts, Wurtzlite, Gilsonite and Montan wax, can also be emulsified by known methods with the aid of cationic salt emulsifiers according to this invention and then can be used effectively as "sizing emulsions."

Of course, other conventional emulsion additives, and in partciular stabilizers often required because of the sensitive stability of cationic bituminous (asphalt) emulsions may be present in conventional small amounts, provided they do not adservely affect the formation and qualities of the ultimate paper and board products.

The emulsified bituminous size in the form of a cationic oil-in-water type emulsion is added and thoroughly intermixed with the pulp in a usually known manner before admitting the thus sized pulp into the paper (or board)-forming machine such as Fourdrinier wires, cylinders, etc., where the size pulp is formed in accordance with known techniques into the utimately desired form of manufactured sheets of paper or board. The size is added at any point of the manufacturing process from the beaters on to the head box in an amount specified to be desirable in a particular ultimate paper or board product. The consistency of the pulp which leaves the head box may vary in a wide range, usually from 0.1 to 0.5% fibrous solids, when paper or paperboard is the ultimate product, and usually from 1 to 3% of fibrous solids, when structural board is to be formed. Somewhat lower and higher consistencies may at times be employed, but as a general rule consistencies above 6% of fibrous solids create pumping troubles and other processing difficulties.

As mentioned hereinbefore, the cationic bitumen-in-water emulsions prepared in accordance with the present invention possess substantivity, that is, they are capable of sizing the fibers without the need for a flocculent or setting agent. When a cationic bituminous emulsion, for instance, an emulsion of asphalt-in-water prepared with a salt of a C_8–C_{20} alkylene diamine described hereinbefore, as an emulsifying agent, is added to the pulp, the particles of asphalt are attracted to the surface of cellulosic fibers because of the opposite electrical charges, and a substantially complete retention of asphalt by the fibers is assured.

The improvements resulting from the use of cationic bituminous emulsions to size the pulp about to be processed to paper or board are illustrated, for instance, by the following data of the preparation of paper handsheets.

The pulp stock was produced from wood by the "soda-sodium sulfide" process, the suspension in water of the resulting "kraft" pulp stock having the consistency within the range of from 0.1 to 0.5% by weight of the cellulosic fibers, commonly used in the industry. The pulp was then beaten, formed into sheets and tested for strength and other properties. Equal proportions of the pulp stock were placed into standard molds of a Hermann handsheet tester. The contents of one mold (blank) were beaten and processed without addition of either the size or the flocculent. In another mold, 7% by weight of asphalt size from a cationic emulsion thereof (about 58% residue) in water was incorporated into the stock. The asphalt was a solvent-refined asphalt from a California crude oil having a penetration of 0 at 77° F. and a softening point of 190° F. It was emulsified with the aid of 1.0% by weight of "Duomeen T" and 1.25% by weight of hydrochloric acid, which formed the corresponding chloride emulsifier. No flocculent was added to the contents of this mold. In a third mold, the same proportion of asphalt size from an anionic emulsion thereof was incorporated into the stock. The asphalt was the same as in the second test mold and has been emulsified in water also in an amount equal to about 58% by weight, using 0.3% by weight of sodium hydroxide and 2.0% by weight of a petroleum-insoluble derivative of pinewood (mainly polymerized abietic acid), known under the trade name of "Vinsol" resin, to provide sufficient anionic soap emulsifier. On comparing the wet strength of the beaten, pressed and dried sheets in a Mullen tester, it is observed after 10 minutes of immersion in water that the cationic asphalt size imparts greater wet strength in pounds per square inch (p.s.i.) to the final board product, the pH of the molds varying from a pH of 4 to a pH as high as 10. Also, the water-resistance (sizing) of the board sized with a cationic emulsion of asphalt, as measured by the respective immersion numbers clearly indicate the greater resistance of the boards sized with "cationic" asphalt size. Immersion numbers refer to the amount of water in centigrams picked up by a sheet (6" x 6") on being immersed in water for ten minutes. FIG. 1 and FIG. 2 of the drawing offer visual confirmation of the higher water resistance and superior wet strength of the board sized with "cationic" bituminous size. In addition, it is observed that the "drain time" (drainage of water) is much faster with pulps sized with "cationic" asphalt size.

If desired, and following the precepts of the earlier paper and board manufacturing practices, formerly known flocculents (setting aids) may be added to pulp stocks being sized with cationic emulsions of bitumen, and their addition will improve the water resistance of the ultimate paper or board products, but as mentioned already the quantity of the flocculent material now acting mainly as a water repellency aid (for instance, the heretofore almost invariably employed alum) that would be required for obtaining a satisfactory product, will be considerably smaller than in using an anionic bituminous size. Apparently the adherence of water to the surface of the fibers (to the sites of hydroxyl group attachment on the cellulose molecule) by virtue of hydrogen bonding is greatly minimized by the fact of the cationic nature of the bituminous size emulsion used in accordance with the invention, and thus less flocculent need be used.

Papermaker's alum—$Al_2(SO_4)_3 \cdot 18H_2O$—heretofore the most frequently employed flocculent of the paper and board industry, is preferred for use as a water-repellency aid in conjunction with the cationic bituminous sizes in accordance with the invention. However, other materials heretofore used as flocculents, for example, aluminum chloride, sodium aluminate, ferric chloride and the like may be used, whenever their use is warranted, and provided they do not affect adversely the improvement in the processing of the pulp owing to the application of cationic bituminous size, and, furthermore, provided they do not impair the desirable properties of the final paper and board products. Thus, ferric chloride is recommended in place of alum whenever a dark-colored board is desired to be produced, and the application of this known flocculent assures, in addition, formation of a product having greater water resistance and dry and wet strength, particularly when using pulps of a high alkaline pH.

The advantages inuring from the use of cationic bituminous sizes of this invention to the manufacture of paper, paperboard and structural board are many:

First of all, the retention of bitumen is remarkably better than in using anionic bituminous sizes. Greater amounts of bitumen, based on the weight of dry fiber, can be introduced into the pulp. Whereas formerly, at best only up to 15% by weight of bitumen, such as asphalt, could be effectively introduced and retained in the final product, now one is enabled to incorporate as much as 50–60% by weight and even more. This is an important advantage in paperboard products, for instance, those intended for use as underlying felts for linoleum or the like, and in other specialty products (e.g., sound-deadening liners). In the case of structural board, the increased contents of bitumen (asphalt) in the product assures better water resistance and is responsible for better tensile and flexural strengths. In paper and paperboard, the wet strength and sizing are also noted to be markedly enhanced.

The drainage of water from the wires is found to proceed at a much faster rate. This represents a tremendous advantage formationwise, permitting greater production. Furthermore, both the white water (from forming machine) and the press water are much clearer and thus can be used over and over again.

In addition, the cationic nature of the bituminous size permits successful application thereof with sensitive pulp stocks, such as pulps produced by the "soda-sodium sulfide" process for various grades of kraft paper.

Finally, another important advantage is a greater flexibility in the use of flocculents, if and when their use is desired. Whereas heretofore, a flocculent, in particular alum, in general could be added effectively only immediately before the pulp stock arrived to the wires, the point of addition of the flocculent acting now mainly as a water-repellency aid is no longer critical, and this addition may be made at any convenient point of admixture.

Although the classical sequence of addition of the size to the pulp stock first and then adding the flocculent to the resulting mix is still preferred, if so desired, one may now add alum to the cationic bituminous emulsion before introducing this latter into the pulp stock; or yet one may add alum to the pulp first and only then add thereto the bituminous emulsion size. This flexibility in mixing the stock with other processing agents therefor permits obtaining the desired degree of uniform distribution of the principal ingredients without undue loss of time.

The following observations additionally illustrate the advantages resulting from the application of cationic bituminous emulsions for sizing cellulosic fiber pulps which are thereafter converted to sheet-form products, such as paper, paperboard, structural board, and the like.

Structural boards were prepared, sizing the shredded, beaten mechanical pulp in standard Williams molds with an emulsion of a solvent-refined asphalt from a California crude oil in water in such amounts as to introduce into the boards 5, 10 and 25%, respectively, of the asphalt size, based on the weight of dry fiber. The asphalt was characterized by a penetration of 0 at 77° F. and a softening point of 190° F. Emulsification of this asphalt (to a residue of 59% by weight) in water was carried out with the aid of 1.0% by weight of "Duomeen T" and 1.25% by weight of hydrochloric acid. The pH of the resulting emulsion was about 1.0, and the particle size, when examined under a microscope, was less than 5 microns, the average particle size being from about 2 to about 4 microns. The consistency of the pulp was of the order of 2.0%. After adding 0, 5.0, 10.0 and 25.0% by weight of the asphalt emulsion size to the molds and thoroughly stirring, 3% by weight

of alum was added to one set of molds, and 1.5% by weight of ferric chloride to another set of molds. The specimen of pulp which was not sized merely received the addition of 3% alum. Boards were also prepared, sizing the pulp with an anionic emulsion of the same asphalt, prepared with the same "Vinsol" resin soap as before and having about the same asphalt content (residue) of 59% by weight as the cationic size emulsion, so as to provide similar asphalt contents in the boards. Again the same amount (3%) of alum was added in each instance. These various boards were then dried at 300° F. for 3 hours and cured for about 16 hours. Subsequent comparison indicated faster water drain time and an unexpectedly better asphalt retention above 10% solids. It was observed that the differential in the drain time of the "unsized" board, prepared with 3% alum, and the board, sized with a cationic asphalt emulsion to 25% asphaltic solids, and treated with alum, was four times shorter than the differential between the drain time of the "unsized" board and the time required to drain the water from the board sized with an anionic emulsion of asphalt, and treated with alum.

Actually, the application of a cationic asphalt emulsion to size the board to 25% asphaltic solids resulted in the same drain time as the application of an anionic asphalt emulsion to size the board to 5% asphaltic solids. The two curves of FIG. 3 in the attached drawing dramatically illustrate this reduction of drain time, which contributes to a faster, more efficient and more economical formation of the board product.

Finally, a series of comparison tests was carried out in standard molds on handsheets sized with a cationic asphalt emulsion, again similarly prepared with the cation-active chloride of "Duomeen T," and on like sheets sized with a comparable anionic asphalt emulsion prepared with the previously mentioned "Vinsol" resin soap emulsifier. In both emulsions, the asphalt was a solvent-refined asphalt characterized by a penetration of 0 at 77° F. and a softening point of 190° F. The asphalt residue of the emulsion in each case was about 59.0% by weight. The paper handsheets were prepared using 0, 3.5 and 7% asphalt solids, based on the dry fiber, and enough alum to get a mold pH of 4.4. The caliper of the sheets was 6.5, the basis weight varying from 25 to 25.7 points per 1000 square feet. While the wet and dry bursting strengths and the "sizing" (water resistance) were comparable in the sheets sized with either of the two kinds of emulsions, the speed of formation, owing to a faster rate of water drainage, was definitely better for sheets sized with the "cationic" size. At 3.5% of asphalt solids, the speed of formation was 5% faster, and at 7% of asphalt solids, it was 10% faster. Furthermore, above about 5% asphalt solids content, the retention of asphalt was markedly improved, and at a solids content of 7%, the retention was 18% higher than in the case of sheets sized with the anionic asphalt size.

Since the water drains at a faster rate, less steam would be required for drying the webs on the dryer rolls, and this will reduce the cost of manufacturing.

The improvement in the retention of the bituminous (asphalt) size from its cationic emulsions in water was observed in this series of tests by drying the sized board specimens to "bone-dry" state and weighing them. Thereupon the boards were placed into a Soxhlet extractor and subjected to repeated extraction with trichloroethylene, until the solvent withdrawn from the extractor appeared to be clear. The boards were then dried again and weighed. The percentage of extractibles, and thence the retention of asphalt was readily calculated. In all instances, whenever the asphaltic solids content was above about 15%, retention was higher (by as much as 20 to 30%) acterized by penetration of 0 at 77° F. and a softening in the boards sized with the cationic bituminous emulsion, as contrasted with the boards sized with the anionic bituminous emulsion. Flexural and tensile strengths were of the same order of magnitude for both types of structural board. When ferric chloride was employed instead of alum in conjunction with the cationic bituminous size, the boards had a somewhat higher flexural strength and were darker in color. This superior retention of asphalt size is clearly shown by the curves in FIG. 4 of the attached drawing.

Another series of observations revealed similar improvements in the drain time and in the retention of bituminous size due to the application of cationic bituminous emulsions in accordance with the invention in the manufacture of paper and paperboard.

Emulsions were prepared by emulsifying in water a solvent-refined asphalt from a California crude oil characterized by penetration of 0 at 77° F. and a softening point of 190° F. The emulsifier was again a chloride of an oil-soluble C_8–C_{20}-alkylene diamine, namely, a chloride of "Duomeen T." The actual proportions used for effecting emulsification were 1.0% of "Duomeen T" and 1.25% of hydrochloric acid. The properties of the resulting emulsified asphaltic size were the following:

Residue, percent by weight	62.0
Retained at 20 mesh, percent by weight	Trace
Retained at 80 mesh, percent by weight	0.04
Viscosity SSF at 77° F.	22
Settlement, percent by weight, after 7 days	4.8

Handsheets 7-point thick, with a basis weight of 26.1 to 27.5 pounds per thousand square feet, were prepared by sizing thoroughly in a standard mold with this "cationic" size a pulp produced by the soda-sodium sulfide (kraft) process and having a pH of 6.6 at a consistency of 0.23% at the time of addition. Alum and ferric chloride were added, in amounts of 3% and 1.5% by weight, respectively, as water repellency aids.

Again the drain time was markedly shorter (5 to 10%) for paper handsheets sized with this emulsion as compared with handsheets sized with a comparable anionic emulsion. Asphalt retention was also improved.

Ferric chloride, whenever used instead of alum, imparted a better bursting strength (in pounds per square inch in the Mullen test), and yielded a darker product. Sizing, i.e., water resistance, was satisfactory, being of the order of 120 to 130 immersion numbers, corresponding to centigrams of water picked up by a sheet 36" square after 10 minutes of immersion.

A series of tests were also made on handsheets of paper sized with the cationic bituminous (asphalt) size mentioned hereinabove to demonstrate the flexibility of the process using such a size. Whether the addition sequence was: (1) adding the size to the pulp stock, followed by a flocculent material, (2) adding this material to the pulp stock, followed by the size, or (3) adding this former flocculent to the size, and then adding the mixture to the pulp stock, in all cases the drain time, dry and wet bursting strengths and water pick-up were substantially the same. This is shown by the data in the following table:

From the aforegiven illustrative data and the accompanying description, it is evident that the advantages of employing cationic bituminous emulsions, and particularly cationic asphalt emulsions, for sizing paper, paperboard, structural board, and the like sheet-form materials, are many. Among these advantages, the faster rate of water drainage from the sized pulp greatly increases the speed of formation and effects substantial economies of energy (such as steam and gas) required in drying the sheets. Also, the retention of the size (asphalt) is reflected in a greater water resistance and an improved strength (both in dry and wet state) of the final paper and board products. In particular the ability of introducing higher amounts of bituminous size (asphalt) permits production of high strength, water-resistant structural board which lends itself to many practical applications for which this material heretofore could not be used. Specifically, the application of the cationic bituminous size, e.g., in the form of emulsions of asphalt, and without need to resort to a flocculent (alum) permits of imparting neutral pH in manufacturing specialized grades of board, such as backing for aluminum siding.

The aforementioned advantages are secured upon sizing pulp stocks with cationic bituminous emulsions in accordance with the invention, irrespective of the particular nature of paper or board forming machinery, whether involving forming the sheets on wires, on cylinders, or in any other possible manner. Furthermore, these advantages are obtained irrespective of the origin of the pulp stock being sized and subsequently formed, that is, be this a mechanical pulp, a soda pulp, a sulfide pulp, a kraft pulp, or any other chemical or semi-chemical pulp, provided the necessary adjustments of pH of the stock are made, which are compatible with the operation of the process of this invention and have no adverse effect on either the operation or the quality of the ultimate product. Nor does the use of the cationic bituminous size of this invention preclude introduction of conventional additives, such as fillers, dyes, etc., which may be required in the preparation of a particular type of paper or board.

In conclusion, it is to be understood that the preceding description merely illustrates the invention and is not to be construed to limit the scope thereof, as set forth in the claims.

We claim:

1. A process for the manufacture of sized sheets of paper and board from a cellulosic fibrous material, said process consisting essentially of the steps of forming an aqueous pulp of said fibrous material of a consistency from about 0.1 to about 6.0% of fibrous solids and thoroughly intermixing with and throughout said aqueous pulp a cationic oil-in-water type emulsion of asphalt characterized by a penetration of from about 0 to about 30 at 77° F. (ASTM D5–52) and a softening point of about 170 to about 260° F. (ASTM D36–26), said asphalt being emulsified in water with the aid of an oil-soluble, cation-active, emulsifying salt of an alkylene diamine of the general formula $RNHR'NH_2$ wherein R

TABLE I.—EFFECT OF SEQUENCE OF ADDITION OF CATIONIC BITUMINOUS SIZE AND FLOCCULENT TO PULP STOCK

[7-point circular paper hand sheets, about 30 sq. inches in area]

	Cationic Asphalt Size With Alum			Cationic Asphalt Size With Ferric Chloride		
	Size To Stock, Then Alum	Alum To Stock, Then Size	Alum to Size, Then To Stock	Size To Stock, Then $FeCl_3$	$FeCl_3$ To Stock, Then Size	$FeCl_3$ To Size, Then To Stock
Drain Time, in seconds	18	19	18	19	19	18
Dry Mullen (p.s.i.)	97	98	99	100	100	98
Wet Mullen (p.s.i.)	48	49	49	52	53	54
Immersion No.	121	125	124	123	129	121

is an acyclic hydrocarbon group of from 8 to 20 carbon atoms and R′ is an alkylene group of from 2 to 3 carbon atoms.

2. The process as defined in claim 1 wherein said oil-soluble cation-active emulsifying salt is a chloride.

3. The process as defined in claim 1 wherein said oil-soluble cation-active emulsifying salt is a nitrate.

4. The process as defined in claim 1 wherein said oil-soluble cation-active emulsifying salt is an acetate.

5. A process for the manufacture of sized sheets of paper and board from a cellulosic fibrous material, said process consisting essentially of the steps of forming an aqueous pulp of said fibrous material at a consistency from about 0.1 to about 6.0% of fibrous solids and thoroughly intermixing with and throughout said aqueous pulp a cationic oil-in-water type emulsion of asphalt characterized by a penetration of from about 0 to about 30 at 77° F. (ASTM D5–52) and a softening point of about 170 to about 260° F. (ASTM D36–26), said asphalt being emulsified in water with the aid of an oil-soluble, cation-active, emulsifying salt of an alkylene diamine of the general formula $RNHR'NH_2$ wherein R is an acyclic hydrocarbon group of from 8 to 20 carbon atoms and R′ is an alkylene group of 2 to 3 carbon atoms; said process furthermore comprising adding to and intermixing with said aqueous pulp a flocculent in an amount sufficient to impart water resistance to the ultimately manufactured fibrous sheet product; and subsequently forming the cellulosic fibers sized with asphalt and containing the flocculent into manufactured form.

6. The process as defined in claim 5 wherein said flocculent is alum.

7. The process as defined in claim 5 wherein said flocculent is ferric chloride.

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