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BITUMINOUS EMULSION

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This invention relates to bituminous emulsions and their use in waterproofing and sizing paper, paperboard, and the like.

This application is a continuation-in-part of application Serial No. 528,641, filed March 29, 1944, for "Bituminous emulsions," which is now abandoned.

Asphalt and other similar bitumens have long been used for waterproofing paper, paper board, roofing felts, and other felted fibrous articles. One method of employing these bitumens as waterproofing agents consists in saturating the felted article in molten bitumen. This procedure is especially practiced in the manufacture of roofing felts, where the aim is to produce a felted article containing more bitumen than fibrous material. Where the aim is to produce an article containing a small amount of bitumen relative to the fibrous material, methods in which the bitumen is incorporated in the fibrous material prior to the felting or sheeting operation are preferable; a more uniformly bituminized felted article is obtained than is obtained if the felted article is treated with molten bitumen. This use of bitumen, wherein the bitumen is incorporated in the fibrous material prior to the felting operation, is referred to as "sizing," since it is a substitute for the more familiar sizing with rosin.

In the practice of those methods wherein bitumen is incorporated in the fibrous material prior to felting, it has been proposed to incorporate solid comminuted bitumen in the aqueous pulp of fibrous material, as in Perry, United States Patent No. 1,288,158, and it has also been proposed to add an aqueous asphalt emulsion, such as an aqueous clay emulsion of asphalt, as in Kirschbraun, United States Patent No. 1,536,399, to the paper pulp. The mixture of pulp and comminuted bitumen or of pulp and bituminous emulsion is then felted or sheeted in the usual way on a paper-making machine, such as a Fourdrinier machine or a single or multiple cylinder machine.

Methods using bituminous emulsions are more advantageous in that a finer subdivision of the bitumen is obtained and a more uniform dispersion of the bitumen throughout the fibrous material is obtained than is obtained with the use of ordinary comminuted bitumen.

However, even with the use of emulsions, great difficulties are experienced in commercial practice. When the emulsion is added to the aqueous pulp, it must necessarily come into contact with

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delicate machinery. Because of the sticky and plastic character of bitumen, it plugs up the screens of Fourdrinier machines and cylinder machines and impregnates and impairs the felts used to pick up the webs of fibrous material from the Fourdrinier screens and the cylinders, so much so that, despite a long history of development and considerable patenting of the art, the employment of bituminous emulsions prior to our invention had not come into wide use. Its applications have been, until recently, largely confined to specialty products where the machinery used is small or is of a type not easily damaged by sticky bitumen.

Aqueous clay emulsions of asphalt have been proposed as a means of obviating the stickiness of asphalt and, indeed, as long as the asphalt remains emulsified and the emulsion contains a large amount of clay, stickiness is avoided. Nevertheless, when the asphalt is deposited on the fibers, it reverts to its sticky condition and is then subject to all the disadvantages of sticky asphalt. And the clay stabilized asphalt emulsions heretofore used have given a great amount of trouble because of plugging cylinders, Fourdrinier machines and felts used to pick up the wet web.

It is an object achieved by the present invention to produce a bituminous emulsion which can be successfully used as a sizing for paper and other felted fibrous articles.

It is a particular object achieved by the present invention to produce a bituminous emulsion which can be added to fibrous pulp as a sizing to produce a highly waterproof paper or other felted fibrous article while avoiding the troublesome clogging of screens, cylinders, and felts and other difficulties that have in the past beset the use of bituminous sizings.

These and other objects of the invention will be apparent from the following description and the appended claims.

We have discovered that many of the difficulties that have lain in the way of using bituminous emulsions to size paper and the like can be obviated, and a very high quality product can be obtained, by the use as the sizing or waterproofing material of an emulsion of a hard, brittle bitumen having the special properties hereinafter described.

Contrary to the teaching of the art, the conventional melting or softening point and penetration tests are not suitable criteria for selection of the type of bitumen employed according to our

invention. Thus, two bitumens may have the same softening points (ASTM D36–26, ring-and-ball method), yet one bitumen may be sticky, plastic, and unsuitable for the purpose of this invention, while the other bitumen may be brittle, relatively nonplastic, and suitable for the purpose of the invention. Likewise, the bitumen to be used according to this invention cannot be chosen solely on the basis of penetration characteristics (ASTM D5–25).

In selecting the bitumen for use in the invention, the following simple test may be employed: A small quantity of bitumen of about 20 mesh, at a temperature of 77° F., is placed on a piece of white paper lying on a piece of plate glass, also at 77° F., and the bitumen is ground with the flat side of a spatula or knife blade. A suitable bitumen will grind to a powder without sticking to the paper or the grinding instrument and without balling up. A bitumen which is not suitable for the purpose of the present invention will stick to the paper or the grinding instrument and will not reduce to a powder.

As pointed out above, the selection of the bitumen to be used according to our invention cannot be predicated on the softening point and penetration characteristics of the bitumen, but, rather, is based on the crushing on paper test described above. However, said softening point and penetration characteristics are useful guides toward the selection of bitumens which may pass said crushing on paper test. In general, asphalts passing the crushing on paper test will have a 0–5 penetration (ASTM D5–25 77° F., 100-gram load, 5 seconds). With the harder grades of asphalt, it is desirable to modify ASTM D5–25 by employing a temperature of 115° F. and a 200-gram load, instead of the conventional 77° F. and 100-gram load. Under such conditions the operable asphalts generally show a 5–35 penetration. In addition to such penetration characteristics, asphalts passing said crushing on paper test will generally be found to have a 180–240° F. softening point, and we prefer to employ those with a 180–220° F. softening point. Corresponding coal tar pitches passing said crushing on paper test generally have a 165–240° F. softening point (ASTM D36–26) and an ASTM D5–25 (77° F., 100 grams, 5 seconds) penetration of 0–5 and, correspondingly, an ASTM D5–25 115° F., 200-gram, 5-second penetration of 0–40.

As pointed out elsewhere herein, the primary consideration relative to the upper limits of softening point and lower limits of penetration is that the bitumens employed become sufficiently fluid at temperatures prevailing at the dry end of the paper making machine, so that the bitumen may be uniformly distributed throughout the sheet of material and become absorbed by the fibres. With paper making machines in use today, the temperatures prevailing at the dry end are generally in the neighborhood of 240–250° F. Obviously, with paper making machine employing higher temperatures at the dry end, it would be both possible and desirable to employ bitumen of the type herein described having higher softening point and lower penetration characteristics.

The bitumen employed according to our invention, as described above, may be prepared by any of the conventional manufacturing methods. Having set forth the desired property of the bitumen, those skilled in the art can with ease adapt said conventional manufacturing methods to produce the bitumen employed according to our invention. For example, when using asphalt as the bitumen, any of the conventional methods of refining may be used, e. g., steam refining, solvent refining, and air-blowing.

An example of a suitable asphalt is that produced by taking a 50/60 penetration standard paving grade asphalt, which may contain as much as 60% of oil, and steam distilling this asphalt under a high vacuum, e. g., about a 28-inch vacuum (2-inch absolute pressure), for a long period of time, sufficient to remove nearly all of the oil. A satisfactory asphalt of the type employed in our invention has been made in this manner by steam refining the asphalt in a shell still under high vacuum. In a typical case, a 30 to 40% yield of brittle asphalt is produced, based on the paving grade asphalt charged to the still. Different asphalts will require refinement to different softening points to produce asphalts of the desired brittleness; thus, a typical California asphalt steam refined under high vacuum to a softening point of 200° F. was satisfactory. Other asphalts may require refinement to a higher softening point, while some asphalts are suitable although refined to a much lower softening point.

Suitable asphalts of the type employed according to our invention, passing the above-described grinding on paper test, can also be prepared by the solvent refining of asphaltic petroleum oil, according to processes widely known and used in petroleum refining. Such solvent refining which involves the extraction of asphalt is advantageous in connection with the practice of our invention for various reasons, included among which is the easy control of the asphaltic oil content of the asphalt. Solvent extraction of asphalt has been widely described in petroleum refining literature. See, for instance, Abraham, "Asphalts and Allied Substances," D. Van Nostrand Co., Inc., New York, 5th ed., pp. 135–139; "Liquid Propane—Use in Dewaxing, Deasphalting and Refining Heavy Oils," R. E. Wilson, P. C. Keith, Jr., and R. E. Haylett, J. Ind. Eng. Chem. 28, 1065 (1936).

Among the solvents employed in the solvent extraction of asphalt are liquid sulfur dioxide; liquid hydrocarbons, such as liquefied ethane, pentane, propane, butane; benzol; toluol; furfural, etc., and mixtures of such solvents as, for example, propane with cresol. In general, liquid propane has been found to be the most satisfactory solvent in connection with the solvent extraction of asphalt. In a typical propane process, propane is liquefied by compression and passed to the bottom of a deasphalting tower where it flows upward countercurrently to descending reduced-asphaltic crude oil. The liquid propane dissolves the non-asphaltic portion of the oil and preferentially precipitates the asphalt. The deasphalted oil is withdrawn overhead and the asphalt is removed from the bottom of the tower. At propane temperatures in the range of 100–150° F., asphalt is only slightly soluble in the propane, whereas the remaining components of the reduced-asphaltic crude oil are largely soluble therein at such temperatures. To extract the asphalt from the reduced crude, the reduced crude is usually mixed with 4 to 6 times its volume of liquid propane at 120–150° F. Pressures employed are those required to maintain the solvent in a liquid state, and range from about 100–350 pounds per square inch absolute.

Oil-dissolving properties of liquid propane for the oil components of the reduced crude decrease as the temperature rises above 100° F., and it is accordingly possible to regulate the physical properties of the precipitated asphalt by varying the

severity of the oil-dissolving step. Typical asphalt recoveries by the propane extraction process are set forth in tabular form below.

Table

Charging Stock	Ratio Solvent to Charge	Treating Temp., °F.	Pressure, p. s. i. a.	Yield, volume Percent Asphalt	Penetration, ASTM D5-25	Softening Point, ASTM D36-26
Kettleman Crude	5-3	138	310	45	3	161
Do	5-3	125	260	35	0	192
Do	10-1	110	220	25	0	210
50/60 pen. Midway Crude	4-1	140	320	58	0	176
Do	8-1	120	250	45	0	197
Do	10-1	100	220	25	0	240
E. Texas Crude	8-1	158	380	36.8	5	153
Rhodessa (La.) Crude	7.5-1	150	350	19.8	4	172
Hvy. Mid-Continent Crude	8.2-1	161	400	46	4	178

Asphalts of the type employed according to our invention may also be prepared by airblowing asphaltic and non-asphaltic petroleum residues, with or without the aid of catalysts and oxidizing agents, in accordance with techniques familiar to those skilled in the asphalt refining art. Excellent results are obtainable by steam refining a Midway, California asphaltic crude to a 150–160 softening point and to about 0–5 penetration and then airblowing such residue at a temperature of 400–500° F. at the rate of 3–5 cubic feet of air per gallon of charging stock per hour for 16 hours. Naturally, well within the knowledge of those skilled in the art, the length of blowing time and other conditions of operation will vary, in accordance with well-established principles, according to charging stock employed and type of apparatus used.

High melting, brittle coal tar pitches, passing the above-described paper crushing test, usable in our invention, may be obtained in any of the usual coal tar pitch production methods, such as in horizontal coke ovens, gas-works retorts, blast furnaces, and the like. Among such coal tar pitches successfully employed according to our invention are those having an ASTM D36–26 softening point of 165–240° F. and an ASTM D5–25 penetration of 0–5, and a penetration of 0–40 at 115° F., 5 seconds, with a 200-gram load. An ASTM D402 Method distillation of such pitches usually gives only a trace of distillate.

Having selected an appropriate bitumen, an emulsion may be prepared in any suitable way. Various types of emulsifying apparatus and various emulsification procedures may be used. In the case of an asphalt, if the asphalt is of the type amenable to emulsification with hot, dilute aqueous caustic alkali in the manner of Montgomerie U. S. Patent No. 1,643,675, or Braun U. S. Patent No. 1,737,491, to produce a quick-setting emulsion, such an emulsion may be prepared. Ordinarily, however, an added emulsifying agent will be required. This may be any of the available emulsifying agents, such as a soap or a protein. Thus, the common soaps, clay, casein, de-fibrinized blood and soya bean meal may be used. High melting, non-sticky emulsifying agents are preferred; that is emulsifying agents which, when the emulsion has been mixed with fibrous pulp and flocculated and the pulp then comes into contact with the cylinders, screens, and felts of a paper machine, will not render the bitumen sticky. The water- soluble soaps of high melting saponifiable materials, such as high melting rosins, are examples of the preferred emulsifying agents. The most advantageous emulsifying agents of the invention are the alkali metal soaps, particularly the sodium soap of a resin of the type described in Lane U. S. Patent No. 2,114,393, and Hall U. S. Patent No. 2,193,026. It is obtained from the wood of Southern long-leaf pine and is a hard, high melting, dark colored resinous material black in color when viewed by light transmitted through a film of the resin. Its use as an emulsifying agent is described in Buckley U. S. Patent No. 2,256,886.

In an illustrative case, a high melting, brittle asphalt or pitch and an aqueous solution of the sodium soap of a resin of the type described in the Lane and Hall patents are fed to a colloid mill (such as the colloid mill of Everett, U. S. Patent No. 2,260,834) in suitable proportions, such as 50 parts bitumen and 50 parts of a 4% aqueous solution of the sodium soap of the resin, parts and percentages being by weight. The bitumen is heated sufficiently to render it freely fluid and the aqueous phase is heated to about 190° F. The colloid mill is so constructed as to allow maintenance of high pressures therein. The components are fed to the mill under sufficient pressure to prevent flashing and boiling of the aqueous phase until the emulsified product has been cooled considerably below the boiling point of the aqueous phase. In most cases the maintenance of a high pressure is important; most of the bitumens used in accordance with the invention are of such high melting point that the mixture of molten bitumen and aqueous phase in the colloid mill is considerably above the boiling point of the aqueous phase. Therefore, unless a sufficient pressure is maintained on the mixture, boiling and flashing will occur. We have found that this boiling and flashing of the aqueous phase are not only inconvenient from an operating standpoint, but the emulsified product is inferior. If boiling or flashing occurs, the particles of bitumen in the product exhibit a "jump grading"; that is, part, and in many cases most, of the bitumen particles, when observed under a microscope, are seen to be of small size, less than 5 microns diameter, but a certain substantial proportion of the bitumen will be present in the form of much larger particles. We believe this is due to the flashing of the aqueous phase, leaving localized areas in which the bitumen is not developed in water, which allows coalescence of small particles or prevents emulsification of the bitumen. In any event, this "jump grading" is disadvantageous if the emulsion is to be added to fibrous pulp as a sizing, because the large particles tend to plug the cylinders, screens, and felts of paper machines. We have found that if pressure is exerted on the bituminous and aqueous components from the

time they are mixed until the emulsion is cooled below the boiling point of the aqueous phase, and preferably to about 150° F., the aforementioned "jump grading" is reduced, and we have also found that it is advantageous to exert a pressure considerably higher than the calculated theoretical pressure just necessary to keep the aqueous phase from boiling and flashing. The emulsion of this invention has at least about 75% of its bituminous material particles of a diameter of about 10 microns or less, and, preferably, 5 microns or less. Before determining the particle size of the dispersed bituminous material, it is customary first to run the emulsion through an ASTM E11–39 40-mesh screen (420 microns) in order not to include any large, coarse particles picked up in the transmission lines, etc. In the preferred method of emulsification, a pressure is exerted sufficient to yield such a product; to prevent the aforementioned "jump grading" and to allow production of an emulsion in which at least 75% of the number of asphalt particles are 5 microns in diameter or less after the emulsion has been screened through a 40-mesh (i. e., 420 micron) screen (ASTM E11–39).

Emulsions so produced or produced by any other suitable method from the above-described bituminous material have very remarkable properties. Thus, if the emulsion is desiccated at room temperature, say about 77° F., it will be found that the residue, unlike the residue of bituminous emulsions heretofore known, is dry, and, upon being stirred up with distilled water, it redisperses to give an emulsion; the dry residue can be re-emulsified merely by stirring with a glass rod or rubber policeman.

The emulsions of the invention may contain 30% or less to 70% or more of bitumen by weight based on finished emulsion, preferably 50 to 60%.

The emulsion so produced is capable of use, not only in sizing or waterproofing paper, but also as a resin extender. Thus, the emulsion may be mixed with an aqueous paste of starch and water-soluble urea-formaldehyde resin, a setting agent for the resin (such as ammonium chloride) being added also, and the mixture may be used as a paper or plywood adhesive. Its most advantageous present use, however, is in sizing or waterproofing paper and the like. Not only is the aqueous emulsion useful, but the dry, friable, dispersible bituminous residue obtained by evaporating the aqueous phase of the emulsion at normal atmospheric or slightly elevated temperatures is also useful. It may, for example, be compressed into bricks, shipped to the point of use (thus saving freight charges on the water) and there mixed with water to produce an emulsion or directly incorporated into an aqueous pulp.

In making paper and other felted fibrous articles, the emulsions of the present invention may be used wherever asphalt emulsions have been used heretofore, as in coating the surfaces of webs as they come from the cylinders of a multicylinder machine to be pressed together and dried after application of the emulsion, thereby forming a multi-ply product with asphalt between the plies to act as an adhesive and waterproofing agent. However, the emulsions of this invention are peculiarly adapted to incorporation in the fiber before the felting or sheeting operation. In so using the emulsions of the present invention, the bituminous emulsion is added to the aqueous pulp of fibrous material which forms the "stock" from which paper, paper board and other felted fibrous articles are made. The emulsion may be added at any stage to the pulp, as to the beater or jordan, and it is thoroughly mixed with the stock. Preferably, the emulsion is added to the stock after the preliminary beating has taken place, but before the final refinement in the jordan. The emulsion is added in amount sufficient to provide the desired amount of bitumen in the finished product. If waterproofness equal to that of ordinary rosin sized paper board is desired, the product will contain about 2% and even as low as 1% of bitumen based on dry paper board. If a highly waterproof paper board is desired which will stand immersion in water for 24 hours or longer, about 10% of bitumen based on dry board will be desired. In manufacturing paperboard products for use as leather substitutes, e. g., box toes and mid-soles for shoes, as much as 30% of bitumen based on dry paperboard will be desired. The bituminous emulsion will be added to the stock accordingly.

Preferably, before the mixture of stock and emulsion is supplied to the web-forming mechanism, an agent is added to flocculate the bitumen and fix it on the fibers. This is conveniently accomplished by adding alum to flocculate the bituminous particles. Alum in quantity sufficient to produce a final pH in the stock of about 4.5 to 5 is preferably added for this purpose. Or the pH of the stock may be adjusted to about 6 by addition of hydrochloric or sulfuric acid and alum added in quantity sufficient to take the pH to 4.5 to 5. Other flocculants than alum may be added; for example, sodium silicate.

The stock is then felted by passing it through a paper forming machine, such as a Fourdrinier machine or a single or multiple cylinder machine and the felted product is dried, all in the usual way. In the drying operation the felted product will ordinarily be (and should be) passed over rolls heated sufficiently to soften the bitumen and cause it to be absorbed by the fibers, thus more thoroughly waterproofing them.

In one form of the invention, as it relates to making felted products, the felted product is formed upon a multiple cylinder machine, the outer cylinders being supplied with ordinary rosin sized stock and the inner cylinders being supplied with stock containing our emulsion. The outer webs of the product are, therefore, ordinary rosin sized webs, while the inner webs contain bitumen. Upon drying and heating the product, the bitumen particles contained in the inner webs will melt and be absorbed by the individual fibers and will also serve to bind the various webs together.

As stated, the finished fibrous product may contain 1 to 30% by weight, based on the dry product, of bitumen, depending upon the desired degree of waterproofness.

The following specific examples will serve further to illustrate the practice and advantages of the invention.

Take a hard, brittle asphalt (having a 190/200° F. softening point by ASTM ring-and-ball method, having a 0 to 5 penetration at 77° F. by ASTM D5–25 method and passing the above-described spatula test wherein the asphalt is ground with a spatula at 77° F.) in the amount of 50 to 55 parts by weight and 50 to 45 parts by weight of a 2% (by weight) aqueous solution of the sodium soap of the pinewood resin of the Lane and Hall patents, referred to above, containing an excess of alkali. Heat the asphalt to 350 to 375° F. and the aqueous solution to 195° to 200° F. Feed the molten asphalt and hot aqueous solution, in the proportions given, to a colloid

mill, such as the Everett colloid mill. This mill may be steam jacketed to maintain the contents sufficiently fluid and it is maintained under a back pressure of 70 to 75 pounds per square inch gauge. The emulsified mixture is passed through a heat exchanger while still under pressure and is cooled to 140° F. before release of pressure.

An emulsion so produced was screened through a 40-mesh screen, examined under a microscope and found to contain the following assortment of particle sizes: ⅓ of particles less than 2 microns in diameter, one-half of particles 2 to 5 microns in diameter, and the remaining one-sixth of the particles 5 to 10 microns in diameter.

Many such emulsions have been used to size paper for making waterproof paper board containing 7.5 to 10% by weight of asphalt based on dry paper board. Thus, in one case the emulsion was used to size chip stock from reclaimed fiberboard boxes. The machine used was a multiple cylinder machine. Alum was added to the stock to flocculate the bituminous sizing and the stock was passed through the machine. Paper so made, containing 10% of asphalt, dry basis, was combined into five-ply paper board, using a waterproof adhesive to cement the plies together. The board so produced had a dry mullen strength of 748 pounds. After 24 hours immersion in water, the mullen strength (i. e., wet mullen strength) had increased to 900 pounds; after seven days immersion, the mullen strength was 780 pounds, still above the dry mullen strength. Only after 30 days immersion was the mullen strength less than the original dry mullen strength, and even then the mullen strength was 90% of the original mullen strength.

By way of contrast, five-ply paper board made in exactly the same way from the same stock, but sized with 3½% of rosin size, based on weight of dry board (3½% of rosin sizing is about the maximum allowable rosin sizing, which is limited by excessive foaming caused by heavy rosin sizing), would have a dry mullen strength of about 650 pounds which, after 24 hours immersion, would be reduced to about 350 pounds.

In another case, paper was made on a seven cylinder machine, the two outer cylinders being supplied with rosin sized stock and the five inner cylinders with stock sized with an asphalt emulsion of the invention. The paper was combined into five-ply board, using a waterproof adhesive to cement the plies together. The inner webs of each ply contained 10% of asphalt; each entire ply, including the outer rosin sized webs, contained 7.5% asphalt. The five-ply board, therefore, contained about 7.5% asphalt. The dry mullen strength of this board was 840 pounds and it contained 7.1% moisture. After 24 hours immersion in water at 70° F., the wet mullen strength was 983 pounds and moisture content was 20%; after 48 hours immersion, 980 pounds mullen strength and 24.4% moisture; and after 7 days immersion, 830 pounds mullen strength and 37.6% moisture.

The advantages of using the emulsions of this invention to size or waterproof felted fibrous articles are manifold. Experience with asphalt emulsions in the sizing of paper has been a story of repeated effort and failure because of the tendency of asphalt to interfere with the operations of the delicate instrumentalities of paper making machines, both of the cylinder (multiple cylinder and single cylinder) type and the Fourdrinier type. This problem has been solved by the method and products of the invention in a most satisfactory way, resulting in large scale sizing of paper with asphalt and other bitumens where before the paper industry avoided the use of asphalt. The product is highly satisfactory and can be made to correspond to ordinary rosin sized paper, to heavily rosin sized paper, and to paper which is waterproofed far beyond the capacity of rosin sizing. And most surprising of all, perhaps, the use of our emulsions offers substantial advantages over rosin sizing from an operating standpoint. Thus, our emulsions cause or permit better web formation on the screens or cylinders of a machine than rosin sizing; rosin sizing interferes with proper web formation because of its tendency to cause foaming, whereas, our bituminous sizing does not cause foaming. Also, higher machine speeds are allowable when our emulsions are used than are allowable with rosin sizing. Our emulsions allow a longer felt life than is possible in making highly rosin sized paper; the rosin size has a greater tendency than the bituminous sizing to penetrate and plug the felts used to pick up and dry the wet webs. An the paper of the invention has greater uniformity across the width of the machine than rosin sized paper.

We claim:

1. An aqueous alkaline bitumen-in-water type emulsion of a bituminous material selected from the group consisting of hard, brittle asphalts having a 0–5 penetration (ASTM D5–25 at 77° F., 100 grams, 5 seconds) and a 180–240° F. softening point (ASTM D36–26) and hard, brittle coal tar pitches of 165–240° F. softening point (ASTM D36–26), said bituminous material being of such hardness that when ground at 77° F. it will reduce to a powder and will not stick to the surfaces which it contacts during grinding, said emulsion having at least about 75% of the bituminous material particles of such size distribution that substantially none exceeds 10 microns in diameter and containing as an emulsifying agent an alkali metal salt of a hard, high-melting petroleum-hydrocarbon-insoluble, alcohol-soluble solvent-extracted pinewood resin.

2. An aqueous alkaline bitumen-in-water type emulsion of a bituminous material selected from the group consisting of hard, brittle asphalts having a 0–5 penetration (ASTM D5–25 at 77° F., 100 grams, 5 seconds) and a 180–240° F. softening point (ASTM D36–26) and hard, brittle coal tar pitches of 165–240° F. softening point (ASTM D36–26), said bituminous material being of such hardness that when ground at 77° F. it will reduce to a powder and will not stick to the surfaces which it contacts during grinding, said emulsion having at least about 75% of the bituminous material particles of such size distribution that substantially none exceeds 10 microns in diameter and containing as an emulsifying agent the sodium salt of a hard, high-melting petroleum-hydrocarbon-insoluble, alcohol-soluble, solvent-extracted pinewood resin.

3. An aqueous bitumen-in-water type emulsion of a bituminous material selected from the group consisting of asphalts having a 0–5 penetration (ASTM D5–25 at 77° F., 100 grams, 5 seconds) and a 180° F.–240° F. softening point (ASTM D36–26) and hard, brittle coal tar pitches of 165–240° F. softening point (ASTM D36–26), said bituminous material being of such hardness that when ground at 77° F. it will reduce to a powder and will not stick to the surfaces which it contacts during grinding, said emulsion having at least about 75% of the bi-

tuminous material particles of such size distribution that substantially none exceeds 10 microns in diameter and being of such character that when dried at room temperature the residue will readily redisperse upon being lightly stirred with water.

4. An aqueous bitumen-in-water type emulsion of a bituminous material selected from the group consisting of hard, brittle asphalts having a 0–5 penetration (ASTM D5–25 at 77° F. 100 grams, 5 seconds) and a 180–240° F. softening point (ASTM D36–26), and hard, brittle coal tar pitches of 165–240° F. softening point (ASTM D36–26), said bituminous material being of such hardness that when ground at 77° F. it will reduce to a powder and will not stick to the surfaces which it contacts during grinding, said emulsion containing the sodium soap of a hard, high-melting petroleum-hydrocarbon-insoluble, alcohol-soluble solvent-extracted pinewood resin as emulsifying agent, and having at least about 75% of the bituminous material particles of 5-micron diameter or less, and containing 30 to 70% by weight of bituminous material based on finished emulsion.

5. An aqueous bitumen-in-water type emulsion of a bituminous material selected from the group consisting of hard, brittle asphalts having a 0–5 penetration (ASTM D5–25 at 77° F., 100 grams, 5 seconds) and a 180–240° F. softening point (ASTM D36–26) and hard, brittle coal tar pitches of 165–240° F. softening point (ASTM D36–26), the selected bituminous material having such hardness and brittleness characteristics that when cooled to 77° F. and having a particle size of about 20 mesh, is placed on a piece of white paper supported by a glass plate and ground with a flat blade, will not stick to the paper or the blade, and will not ball up under the blade, said emulsion having at least about 75% of the bituminous material particles of such size distribution that substantially none exceeds 10 microns in diameter.

6. An aqueous bitumen-in-water type emulsion of a bituminous material selected from the group consisting of hard, brittle asphalts having a 0–5 penetration (ASTM D5–25 at 77° F., 100 grams, 5 seconds) and a 180–240° F. softening point (ASTM D36–26) and hard, brittle coal tar pitches of 165–240° F. softening point (ASTM D36–26), the selected bituminous material having such hardness and brittleness characteristics that when cooled to 77° F. and having a particle size of about 20 mesh, is placed on a piece of white paper supported by a glass plate and ground with a flat blade, will not stick to the paper or the blade, and will not ball up under the blade, the bituminous material in the emulsion being of such size distribution that not more than 25% exceeds 5 microns in diameter.

7. An aqueous bitumen-in-water emulsion of a bituminous material selected from the group consisting of hard, brittle asphalts having a 0–5 penetration (ASTM D5–25 at 77° F., 100 grams, 5 seconds) and a 180–240° F. softening point (ASTM D36–26) and hard, brittle coal tar pitches of 165–240° F. softening point (ASTM D36–26), in which emulsion not more than 25% of the bitumen particles exceed 5 microns in diameter, said bitumen being of such hardness that when ground at 77° F., it will reduce to a powder and will not stick to the surfaces which it contacts during grinding, the softening point of said bitumen being such that, when the emulsion is mixed with an aqueous fibrous pulp, alum is added to the mixture of emulsion and pulp to cause flocculation of the bitumen on the fibers, and the flocculated mixture is formed into a fibrous sheet and passed through heated rolls at about 240° F., the bitumen will flow freely and coat the fibers uniformly.

8. An aqueous bitumen-in-water type emulsion of a bituminous material selected from the group consisting of asphalts having a 5–35 penetration (ASTM D5–25 at 115° F., 200 grams, 5 seconds) and a 180°–240° F. softening point (ASTM D36–26) and hard, brittle coal tar pitches of 165–240° F. softening point (ASTM D36–26), said bituminous material being of such hardness that when ground at 77° F. it will reduce to a powder and will not stick to the surfaces which it contacts during grinding, said emulsion having at least about 75% of the bituminous material particles of such size distribution that substantially none exceeds 10 microns in diameter and being of such character that when dried at room temperature the residue will readily redisperse upon being lightly stirred with water.

9. An aqueous bitumen-in-water type emulsion of a bituminous material selected from the group consisting of hard, brittle asphalts having a 5–35 penetration (ASTM D5–25 at 115° F., 200 grams, 5 seconds) and a 180–240° F. softening point (ASTM D36–26) and hard, brittle coal tar pitches of 165–240° F. softening point (ASTM D36–26), the selected bituminous material having such hardness and brittleness characteristics that when cooled to 77° F. and having a particle size of about 20 mesh, is placed on a piece of white paper supported by a glass plate and ground with a flat blade, will not stick to the paper or the blade, and will not ball up under the blade, said emulsion having at least about 75% of the bituminous material particles of such size distribution that substantially none exceeds 10 microns in diameter.

10. An aqueous bitumen-in-water emulsion of a bituminous material selected from the group consisting of hard, brittle asphalts having a 5–35 penetration (ASTM D5–25 at 115° F., 200 grams, 5 seconds) and a 180–240° F. softening point (ASTM D36–26) and hard, brittle coal tar pitches of 165–240° F. softening point (ASTM D36–26), in which emulsion not more than 25% of the bitumen particles exceed 5 microns in diameter, said bitumen being of such hardness that when ground at 77° F., it will reduce to a powder and will not stick to the surfaces which it contacts during grinding, the softening point of said bitumen being such that, when the emulsion is mixed with an aqueous fibrous pulp, alum is added to the mixture of emulsion and pulp to cause flocculation of the bitumen on the fibers, and the flocculated mixture is formed into a fibrous sheet and passed through heated rolls at about 240° F., the bitumen will flow freely and coat the fibers uniformly.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,511,949	Commin	Oct. 14, 1924
1,722,434	Kirschbraum	June 30, 1929
2,003,860	McConnaughay	June 4, 1935
2,190,034	Levin	Feb. 13, 1940