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2,972,588

STABLE TAR-IN-WATER DISPERSIONS AND
METHOD FOR PREPARING SAME

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This invention relates to stable tar-in-water emulsions or dispersions and more particularly pertains to compositions comprising dispersions of finely-divided tar particles in water and to the method for preparing said compositions.

This invention is concerned with novel emulsions or dispersions in which tar is the dispersed phase and water is the continuous phase said emulsions or dispersions having unusual resistance to creaming or settling and to coalescence or coagulation of the dispersed phase.

The tar embodied in the present invention is the liquid, semi-liquid or solid thick brown to black substance with a distinctive odor obtained by the distillation of wood, peat, coal and other vegetable matter. The most commonly used tars of the type embodied in this invention are those known as "coal tar" and "wood tar." These tars are to be distinguished from the petroleum based asphalts. The preferred tars for the purpose of this invention are the road tars, known as RT, in the viscosity range of RT-1 to RT-12, inclusive.

Tar is an excellent material for use in the building trade and in road and airport runway surfacing. Tar has an advantage which asphalt does not have, namely, insolubility or inertness to gasoline, kerosene and petroleum oils in general. This advantage is a real one, especially in the road surfacing industry where accidentally spilled fuels and oils can cause serious damage to many types of road surfaces. Tar has been applied to road surfaces in the molten state. This is generally undesirable. Tar dispersions suitable for use in the building and the road construction and maintenance trades have not been available heretofore because of the hydrophobic nature of tar and the lack of natural emulsifying and dispersing agents in tar. Tar-in-water dispersions which have been prepared and used prior to my invention have contained relatively large amounts of emulsification agents of the fatty acid and lignin types and hydrophilic fillers such as clay. They have been relatively unstable to aging, and films formed from the tar dispersions of the prior art exhibit inferior physical properties and in particular a high degree of water-sensitivity by virtue of the residual emulsification agents and hydrophilic fillers present in said films. The prior art tar dispersions have not exhibited the proper stability, that is, many of them tend to cream or settle upon standing, so that an agitation or homogenization step is required prior to and even during their application to a surface. The tar-in-water dispersions of this invention can be deposited or coated at moderate temperatures on surfaces to form continuous tar films which are of low water sensitivity. Such dispersions can be applied to roads, for example, to provide surfaces impervious to gasoline, petroleum oils and greases of the types which occasionally drip from or are accidentally spilled from motor vehicles. Such surfaces are also unaffected by atmospheric moisture or natural precipitation.

Accordingly, an object of the present invention is the provision of tar-in-water dispersions which can be pre-

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pared with or without extraneous fillers and which remain homogeneous for extended periods of time in storage containers. Another object is the provision of high solids, stable tar-in-water dispersions which have a wide range of viscosities. Still another object is the provision of stable tar-in-water dispersions which form coatings and deposits of tar upon the evaporation of the water phase said coatings and deposits exhibiting a negligible degree of water-sensitivity. Another object is the provision of a method for preparing said stable tar-in-water dispersions.

Still further objects and advantages of the present invention will appear from the more detailed description and examples set forth below, it being understood that such detailed description is given by way of illustration and explanation only, and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the invention.

I have discovered a novel stable composition comprising at least 35 parts by weight of water, up to about 65 parts by weight of finely dispersed tar and a minor proportion of a synthetic, lightly cross-linked, water-swella-ble, carboxyl containing polymer and sufficient neutralizing agent to impart a pH of from about 5 to about 8.

The tar-in-water dispersions embodied in the present invention can be prepared by homogenizing in any desired order the aforementioned tar, synthetic, lightly cross-linked, water-swella-ble, carboxyl containing polymer, neutralizing agent and water.

The synthetic, lightly cross-linked, water-swella-ble, carboxyl containing polymers embodied in this invention are useful in the range of from 0.05 to 2% by weight and, preferably, from 0.06 to 1.5% by weight based on the weight of tar. These polymers include interpolymers of at least 20% by weight of an alpha, beta-olefinically unsaturated carboxylic acid or anhydride thereof, up to about 80% by weight of another mono-olefinic monomer copolymerizable therewith and from about 0.01 to about 10% and more preferably 0.01 to about 5% by weight based on the total weight of monomers of an olefinic monomer having at least two polymerizable olefinic groups in each molecule. It is to be understood that in the above proportions, if a maximum amount of two of the monomers are utilized that somewhat less than maximum amounts of the other monomers must be utilized.

It is to be understood also that the water-swella-ble carboxyl containing polymers can be composed of only two essential ingredients, the polymerizable acid and a cross-linking ingredient, which is the olefinic monomer having at least two polymerizable olefinic groups in each molecule.

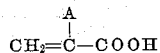
In the alpha, beta-olefinically unsaturated acids the close proximity of the strongly polar carboxyl group or carboxylic anhydride group to the double bonded carbon atoms has a strong activating influence rendering the substances containing this structure very readily polymerizable. Representative monoolefinically unsaturated monocarboxylic acids useful for preparing the cross-linked interpolymers of this invention include acrylic acid, methacrylic acid, ethacrylic acid, alpha-fluoro, chloro, bromo and iodo acrylic acids and crotonic acid or anhydrides of one or a mixture of the above acids.

Representative monoolefinically unsaturated polycarboxylic acids include maleic acid, fumaric acid, citraconic acid, mesaconic acid, glutaconic acid or anhydrides thereof and halogen substituted derivatives of these acids or anhydrides.

Representative polyolefinically unsaturated monocarboxylic acids are pentadiene-2,4-oic acid, sorbic acid, an-

hydrides thereof and halogen substituted derivatives.

The preferred alpha, beta-olefinically unsaturated carboxylic acids for use in this invention are the monoolefinic acrylic acids having the structure



wherein A represents hydrogen, halogen and a lower alkyl group. Illustrative acrylic acids of this preferred class are acrylic acid itself, methacrylic acid, ethacrylic acid, and a substantially equimolar mixture of maleic anhydride and another monomer copolymerizable therewith. Of this class, acrylic acid itself is most preferred because of its generally lower cost, ready availability, and ability to form superior polymers.

The swelling capacity (or swelling index) of the lightly cross-linked interpolymers depends primarily upon the carboxyl groups in the interpolymer chain, therefore, it is generally desirable to utilize as much of the carboxylic monomer or monomers and as little of the other monomeric constituents as is consistent with the necessary water sensitivity, dispersibility, emulsification, suspension, thickening and other desirable properties. In these interpolymers the carboxylic monomer or monomers should never be less than 20% by weight of the total monomeric mixture.

Additional monomers suitable for the production of multi-component interpolymers, as above described, are monoolefinic monomers such as the fluoro-, chloro-, bromo-, iodo- and ethoxy styrenes, nuclear sulfonated styrenes, acrylamide, methacrylamide, N,N-dimethyl acrylamide, N-methyl methacrylamide, acrylonitrile, methacrylonitrile, vinylidene cyanide, methyl acrylate, ethyl acrylate, propyl acrylates, butyl acrylates, amyl acrylates, hexyl acrylates, cyclohexyl acrylate, heptyl acrylates, octyl acrylates, methyl methacrylate, methyl ethacrylate, vinyl acetate, vinyl propionate, vinyl butyrate, isopropenyl acetate, isopropenyl propionate, isopropenyl butyrate, vinyl benzoate, isopropenyl benzoate, vinyl pyridines, vinyl chloride, vinyl bromide, vinyl fluoride, vinylidene chloride, vinylidene bromide, vinylidene fluoride, vinylidene chlorobromide, vinyl carbazole, vinyl pyrrolidone, vinyl piperidines, vinyl pyrimidines, methyl vinyl ketone, ethyl vinyl ketone, methyl isopropenyl ketone, ethylene, propylene, dimethyl maleate, diethyl maleate, dimethyl fumarate, diethyl fumarate, methyl vinyl ether, ethyl vinyl ether, the propyl vinyl ethers, the butyl vinyl ethers, cyclohexyl vinyl ether, phenyl vinyl ether, allyl acetate, allyl propionate, allyl benzoate, isobutylene, and other monomeric substances which are copolymerizable with the alpha, beta-olefinically unsaturated carboxylic acid. Of the above additional monomers N-methyl acrylamide, acrylonitrile, methyl vinyl ether, vinyl acetate, isobutylene and styrene have been found particularly useful for the production of water-swelling interpolymers. Interpolymers can be made from mixtures of maleic anhydride, a vinyl alkyl ether such as methyl vinyl ether, and a cross-linking agent as herein defined in which the sum of the moles of vinyl ether is substantially equivalent to the molar quantity of maleic anhydride present.

The cross-linking agents useful in the practice of this invention are olefinic monomers having at least two polymerizable olefinic groups per molecule. The cross-linking agents embodied in this invention include such compounds as divinyl benzene, nuclear substituted divinyl benzenes, di-isopropenyl benzene, trivinyl benzene, nuclear substituted trivinyl benzenes, triisopropenyl benzene, triallyl benzene, 1,6-heptadiene and similar terminally olefinically unsaturated non-conjugated dienes of the type disclosed in the copending U.S. patent application Serial No. 737,541, filed May 26, 1958 by John F. Jones, Alfred J. Mital and Franz A. Regenass, tetravinyl silane, tetraallyl silane, and similar polyalkenyl monomers disclosed in the copending U.S. patent application

of John F. Jones and Alfred J. Mital, Serial No. 701,328, filed December 9, 1957, triacrylyl triazine, trimethacrylyl triazine, methylene-bis-acrylamide, methylene-bis-methacrylamide, hexaallyl trimethylene trisulfone, squalene, myrcene, alkali metal polymerized 1,2-polybutadiene, alkali metal polymerized 1,2- and 3,4-polyisoprene, divinyl spirobi, polyalkenyl polyethers of the type disclosed in U.S. Patent No. 2,789,053, and the like and others.

In addition to the foregoing cross-linking agents other suitable cross-linking agents which contain hydrolyzable linkages can be employed in the production of tar-in-water dispersions in applications where long-term stability is not essential. Such hydrolyzable cross-linking agents include allyl acrylate, methallyl acrylate, crotyl acrylate, and others disclosed in U.S. Patent No. 2,340,111.

The preferred cross-linking agents are the polyalkenyl polyethers, the polyalkenyl silanes and the terminally olefinically unsaturated dienes.

The preferred method of preparation of the water-swelling carboxyl containing polymers embodied in this invention is polymerization in an inert diluent having some solubilizing action on one or more of the monomeric ingredients but substantially none on the resultant interpolymer. Polymerization in mass may be employed, but is not preferred because of the difficulty in working up the solid polymeric masses obtained. Polymerization in an aqueous medium containing a water-soluble free-radical catalyst is useful, the product resulting either as a granular precipitate or as a highly swollen gel, either of which may be used directly or are easily further subdivided and dried. Polymerization in an organic liquid which is a solvent for the monomers but a non-solvent for the interpolymer, or in a mixture of such solvents, in the presence of a solvent-soluble free-radical catalyst such as benzoyl peroxide and azobisisobutyronitrile is most preferred because the product is usually obtained as a very fine friable and often fluffy precipitate which, after solvent removal, seldom requires grinding or other further treatment before use. Suitable solvents for the latter method include benzene, toluene, xylene, ethyl benzene, tetralin, hexane, heptane, octane, carbon tetrachloride, methyl chloride, ethyl chloride, ethylene dichloride, bromotrichloromethane, chlorobenzene, acetone, methyl ethyl ketone, and others, and mixtures of these and other inert solvents.

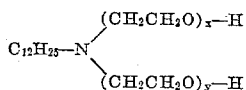
Polymerization in the diluent medium may be carried out in the presence of a free-radical catalyst in a closed vessel in an inert atmosphere and under autogenous pressure, artificially induced pressure or in an open vessel under reflux at atmospheric pressure. The temperature of the polymerization may be carried from 0° C. or lower to 100° C. or higher, more preferably from 20° to 90° C., depending to a large degree upon the activity of the monomers and catalyst used and the molecular weight desired in the polymeric product. The molecular weights of said interpolymers are greater for those made in the lower temperature range than for those made in the higher temperature range. Polymerization at 50° to 90° under atmospheric pressure using a free-radical catalyst is generally effective in producing a polymer yield of 75 to 100% of theory in less than 10 hours, usually in less than 5 hours. Suitable free-radical catalysts include peroxides such as sodium, potassium and ammonium persulfates, caprylyl peroxide, benzoyl peroxide, pelargonyl peroxide, hydrogen peroxide, cumene hydroperoxide, tertiary butyl diperphthalate, tertiary butyl perbenzoate, sodium peracetate, sodium percarbonate, and the like as well as azobisisobutyronitrile and others. Other catalysts utilizable are the so-called "redox" type of catalyst and the heavy-metal activated catalyst systems. Polymerization may be induced by radicals formed in the polymerization system by nuclear radiation, X-rays and ultra-violet radiation.

The neutralizing agent employed in the present inven-

tion for the adjustment of the pH of the tar-in-water dispersions comprises a mixture of (1) a monovalent inorganic alkaline material including ammonia and alkali metal bases such as the hydroxides, oxides, or carbonates and (2) a basic organic amine having at least 6 carbon atoms. The purpose of the neutralizing agent is to swell the synthetic lightly cross-linked water-swellaible carboxyl containing polymer. The greatest degree of swelling of the carboxyl containing polymer occurs in the pH range of from about 5 to about 8. The desired pH range is obtained by neutralizing from about 50 to about 80% of the carboxyl groups present in the polymer. The alkali metal hydroxide, oxide or carbonate forms the alkali metal salt of the carboxyl containing polymer and thus makes the polymer more water sensitive and highly swollen in water. It is believed that the basic organic amine functions to increase the swell of the carboxyl containing polymer and also to make the carboxyl containing polymer compatible with the dispersed tar phase.

The alkali metal hydroxides, oxides and carbonates useful in this invention include sodium hydroxide, sodium oxide, sodium carbonate, sodium bicarbonate, potassium hydroxide, potassium oxide, potassium carbonate, potassium bicarbonate, lithium hydroxide, lithium oxide, lithium carbonate, lithium bicarbonate, rubidium hydroxide, rubidium oxide, rubidium carbonate, rubidium bicarbonate, cesium hydroxide, cesium oxide, cesium carbonate, cesium bicarbonate and the like. The preferred of this group are the sodium and potassium hydroxides and carbonates.

The basic organic amines useful in this invention include the higher aliphatic primary, secondary, tertiary amines and quaternary amine hydroxides and alkylene oxide-treated amines. Specific examples of higher organic amines include n-octyl amine, di-n-octyl amine, tri-n-octyl amine, n-decyl amine, di-n-decyl amine, tri-n-decyl amine, n-dodecyl amine, di-n-dodecyl amine, tri-n-dodecyl amine, stearyl amine ethylene oxide treated dodecyl amine and tetraalkyl ammonium hydroxides such as tetraoctyl ammonium hydroxide and tetradodecyl ammonium hydroxide. The preferred higher organic amines are dodecyl amine and the compound



wherein $x+y$ equals about 15, said compound having a molecular weight of about 875.

The weight ratio of basic organic amine to alkali metal hydroxide, oxide, or carbonate in the aforementioned neutralizing agent can be from about 0.0125:1 to about 0.2:1 respectively.

The tar-in-water dispersions embodied in this invention are most conveniently prepared by adding the acid form of the carboxyl containing polymer to water, mixing with a medium speed Waring Blendor or similar mechanical mixer of the "Lightnin" and Eppenbach types followed by partial neutralization of the polymer to the desired pH with the neutralizing agent. The resulting mucilage is maintained at a temperature of from about 25° C. to about 100° C. while molten tar is added slowly, with continuous stirring, to the mucilage. The tar dispersion can be used hot or it can be cooled and stored for long periods of time without creaming or coagulation. Generally the tar dispersions prepared with high shear mixing tend to be characterized by a fine particle size and are very smooth but dry more slowly when coated on a surface than do the tar dispersions formed with slow speed mixing ("Lightnin" or Eppenbach mixers). The latter dispersions tend to be more grainy but the larger particle size allows fast and even drying of thick films. The tar-in-water dispersions of this invention can be blended with aqueous dispersions of natural or synthetic rubbers, with natural or synthetic rubber latex or with dispersions and emulsions of synthetic plastics and films resulting from

such blends are generally tough and rubbery in nature. The addition of fillers to the tar dispersions generally results in the production of harder films deposited therefrom.

In the preferred method for the preparation of the tar dispersions embodied herein it is important that a relatively slow addition of the tar to the water phase be employed. Preferably, the tar addition is not any faster than the dispersion rate.

When highly viscous road tars (RT-9 to 12) are dispersed, it is preferred to mix the molten tar with a hot water phase wherein the temperature of the tar phase is maintained at 55-130° C. and the water phase is maintained at 55-70° C. and when the addition is completed, the mixing is stopped and the resulting homogeneous dispersion is cooled rapidly without further agitation. The less viscous road tars (RT-1 to 8) and the water phase may be mixed conveniently at normal temperatures.

In the preparation of the tar dispersions it is preferred that a sufficient quantity of neutralizing agents be used in the water phase to impart a pH of from about 5.2 to 7 to the dispersion. Once the dispersion has been prepared the pH may be adjusted to pH value below 5.2 and above 7, if it is so desired, without noticeable effect on the stability of the dispersion.

In the following illustrative examples the amounts of ingredients are given in parts by weight unless otherwise specified.

Example I

A mixture of 300 parts of water, 4.5 parts of a 10% aqueous sodium hydroxide solution, 0.75 part of dodecyl amine (Armeen 12D) and 1.5 parts of an interpolymer of 100 parts of acrylic acid and 1 part of polyallyl sucrose having between 5 and 6 allyl groups per sucrose molecule was stirred gently at 90° C. until thick. It is preferred to partially neutralize the water-swellaible polymer with alkali prior to the addition of the organic amine in order to avoid the possibility of precipitation of the polymer. A sample of 300 parts of RT-12 grade tar of the type widely used in road construction was heated to 130° C. and added slowly to the above-described aqueous gel. The mixing of the aqueous gel and warm tar was conducted with a Waring Blendor at medium speed. The mixing was discontinued as soon as the addition of the tar was completed and the resulting dispersion was cooled to room temperature. A stable, pourable dispersion of tar in water resulted which had fairly fine particle size and a pH of 6.8. The Brookfield viscosity of this 50% tar-in-water dispersion was 4150 centipoises. The tar-in-water dispersion of this example was stable to creaming and coalescence on standing for long periods of time.

When unusually high speed mixing is employed during the addition of the warm tar or when the described Waring Blendor mixing is prolonged after the completion of the addition of the tar, unstable dispersions result.

The stable dispersion described above was coated on a sheet of steel and was allowed to dry. A continuous film of tar was observed on the surface of the steel and this tar film was substantially insensitive to water upon immersion in a water bath for 5 days.

Two 50% aqueous dispersions of RT-12 were prepared in accordance with the teaching of U.S. Patent No. 2,670,332, one was prepared employing a "Lightnin" mixer and the other was prepared by means of a Waring Blendor. The dispersions were excellent in appearance immediately after preparation, but settling of the tar phase to a hard cake was observed in each after a week's standing. In each case the tar cakes were so thick that it was difficult to push a spatula through them. The cakes could, however, be redispersed with a "Lightnin" mixer. Films cast from these original dispersions on steel plates were extremely sensitive to water. Upon immersion of the coated plates in water for one day it was observed that the films absorbed water and completely lost their adhesion to the

plates. The foregoing experiments serve to distinguish the novel tar-in-water dispersions embodied in the instant invention from those of the prior art.

Example II

The procedure described in Example I was followed and the following ingredients were used to prepare the following tar-in-water dispersions:

	A	B	C	D
Water	300	300	300	300
Acrylic acid-1% polyallyl sucrose interpolymer	1.5	1.5	1.5	1.5
Polvethylene oxide modified dodecylamine (Ethomeen C-12)	0.5			
Polvethylene oxide modified dodecylamine (Ethomeen C-25)		0.5		1.13
Quaternary amine hydroxide (Arquad-C-hydroxide, 5% sol. in Alcohol)			1.0	
10% sodium hydroxide solution	4.5	4.5	4.5	4.5
Tar (RT-12)	300	300	300	300
pH	6.5	6.3	6.5	6.5

All of the above dispersions were good. Dispersion D was particularly good in that it was unusually smooth and of fine particle size. All of the above dispersions were stable on aging. Dispersion B, for example, showed no phase separation after aging for one month at 130° C. in a closed container.

The above-described dispersions form excellent smooth coatings on paper with little or no penetration through the paper. Dispersions of the above-described types wherein 2.0 parts of the acrylic acid-polyallyl sucrose polymer were employed are much more viscous and they can be coated on porous surfaces with no penetration into the pores.

Example III

This example illustrates the use of fillers in the tar-in-water dispersions of the present invention. A standard tar-in-water dispersion of the type D in Example II was used in the present example. Each of the fillers was added to the dispersion and mixing was accomplished with a "Lightnin" mechanical mixer. In each case 30% by weight of filler was used based on the weight of the tar present in the dispersion. A control dispersion (A) is included in this example.

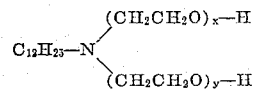
	A	B	C	D
Dispersion	180	180	180	180
Water		27	27	27
Silica flour (100 mesh)		27		
Talc (Asbestine 3X)			27	
Dixie clay				27
Dried films	fairly soft, smooth.	harder, smooth	harder, smooth	hard, somewhat rough.
Original dispersion properties:				
Brookfield (20 r.p.m.) Visc	15,500	16,250	3,000	21,000
pH	6.4	6.4	8.2	6.6
16 Days' aging, dispersion properties:				
Brookfield (20 r.p.m.) Visc	23,500	13,250	2,750	12,500
pH	6.4	6.4	8.2	6.6
Crust on top	slight	no	no	no

Films of the above-described dispersions were cast on aluminum panels. The final thickness of the dried films was about 0.041-0.045 inch. The percent moisture pick-up was determined for these films after air drying for 66 hours to constant weight followed by immersion in water for the indicated number of days.

	Percent Moisture Pickup			
	A	B	C	D
1 day's immersion	1.78	4.25		
7 days' immersion	2.79	4.44		
14 days' immersion	3.14	4.64	2.53	5.13

Example IV

In a manner similar to that described in Example I a tar-in-water dispersion was made from a mixture of 348 parts of distilled water, 0.875 part of an interpolymer of acrylic acid and 1.25% tetravinyl silane, 2.6 parts of 10% aqueous sodium hydroxide, 0.44 part of the compound



wherein $x+y=15$ having a molecular weight of 875 (Ethomeen C-25), and 287 parts of RT-12 tar. The final dispersion had a Brookfield (20 r.p.m.) viscosity of 10% 640 cps. at 25° C. The emulsion was stable in spite of the fact that it had a relatively large particle size.

Example V

A tar-in-water dispersion was prepared according to the procedure outlined in Example I from a mixture of 342.1 parts of distilled water, 1.75 parts of an interpolymer of acrylic acid and 2.5% 1,8-nonadiene, 5.25 parts of 10% aqueous sodium hydroxide solution, 0.88 part of Ethomeen C-25 and 287 parts of RT-12 tar. An excellent dispersion having good stability and a smooth consistency and a Brookfield (20 r.p.m.) viscosity of 9,200 at 25° C. resulted.

Example VI

A tar-in-water dispersion was prepared according to the procedure given in Example I from a mixture of 318.5 parts of distilled water, 7.0 parts of an interpolymer of acrylic acid and 0.2% tetraallyl silane, 21 parts of 10% aqueous sodium hydroxide, 3.5 parts of Ethomeen C-25 and 287 parts of RT-12 tar. An excellent, easily pourable dispersion resulted which had a Brookfield (20 r.p.m.) viscosity of 1,300 cps. at 25° C. This dispersion was of a light brown color and formed smooth coatings on paper. The dispersion had excellent stability to aging.

80 parts of the tar-in-water emulsion described above were blended with 8 parts of a synthetic nitrile rubber latex (an interpolymer of 55% butadiene and 45% acrylonitrile) as follows. The rubber latex and tar emulsion were compatible giving a greenish gray formulation having fair fluidity capable of forming very smooth coatings

on paper and on glass. The films were rubbery, especially when warmed, exhibiting "snap" which tar films do not show. Other types of rubber latexes such as those of the acrylates, styrene-butadiene and natural rubber were used in place of the above-described nitrile latex with comparable results.

Aluminum pigment was incorporated into the tar-in-water dispersion of this example. 6 parts of finely-divided aluminum pigment were blended into 100 parts of the tar-in-water dispersion to give a smooth, silvery formulation which yields metallic appearing films upon drying. These tar- and aluminum-in-water dispersions are excellent for coating roofs and as insulation coatings in building construction and in packaging.

Example VII

A tar-in-water dispersion was made by the procedure given in Example I from a mixture of 342.1 parts of distilled water, 1.75 parts of an interpolymer of acrylic acid and 1% tetraallyl pentaerythritol, 5.25 parts of a 10% aqueous sodium hydroxide solution, 0.88 part of Ethomeen C-25 and 287 parts of RT-12 tar. The cooled dispersion had a viscosity of 23,000 cps. The dispersion was stable and smooth.

In a similar manner a tar-in-water dispersion was prepared from the foregoing ingredients except that a softer tar, RT-8, was substituted for the RT-12. The resulting dispersion was very stable and smooth and it had a viscosity of 58,000 cps. at 25° C.

Example VIII

A number of dispersions were prepared using the procedure described in Example I employing a copolymer of 99.5% acrylic acid and 0.5% tetraallyl pentaerythritol, Armeen C-25, sodium hydroxide and RT-8. The tar phase and the water phase were both maintained at about 25° C. during the addition. The variations in method of preparation and properties of these dispersions are given in the following table.

Percent RT-8	Percent Polymer	pH	Addition Time, minutes	Mixer	Dispersion
53.5	0.22	6.3	4	Waring Blender	Good.
50	0.125	6.9	10	Lightnin	Do.
50	0.063	6.6	6	Eppenbach	Do.
50	0.125	6.25	9	do	Excellent.
50	0.125	9.0	3	do	No good.
63.6	0.091	6.27	19	do	Excellent.

Example IX

A series of dispersions was prepared as described in Example VIII with the exception that RT-12 was used. An addition time of 9 minutes and an Eppenbach mixer were used throughout. The results are listed in the following table.

Percent RT-12	Percent Polymer	pH	Addition Temp.	Dispersion
50	0.125	6.1	25° water 60° tar	Good.
50	0.125	6.15	65° water 60° tar	Do.
50	0.125	6.25	65° water 65° tar	Do.
50	0.125	5.2	50° water 65° tar	Do.
50	0.125	6.4	65° water 65° tar	V. Good.
50	0.125	6.85	65° water 70° tar	Good.
50	0.10	5.2	63° water 75° tar	Do.
50	0.075	5.0	68° water 72° tar	Fair.

I claim:

1. A stable tar-in-water dispersion comprising at least 35 parts by weight of water, up to about 65 parts by weight of homogeneously and finely dispersed coal tar and as the sole emulsifying and dispersing agent from 0.05 to about 2 parts by weight based on 100 parts of said coal tar of a mixed alkali metal base-organic amine salt of a synthetic lightly cross-linked water-swella-
 35
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 65
 70
 75

20% by weight of an alpha, beta-olefinically unsaturated carboxylic acid, (2) up to about 80% by weight of another monoolefinic monomer copolymerizable with (1) and (3) from about 0.01 to about 10% by weight based on the total weight of monomer of an olefinic monomer having at least two polymerizable olefinic groups in each molecule said dispersion having a pH of from about 5 to about 8.

2. The dispersion of claim 1 wherein the coal tar is in the range RT-1 to 12.

3. The dispersion of claim 1 wherein the synthetic lightly cross-linked water-swella-
 15
 20
 25

4. A stable, tar-in-water dispersion comprising at least 35 parts by weight of water, up to 65 parts by weight of homogeneously and finely-dispersed RT-1 to 12 coal tar and as the sole emulsifying and dispersing agent from 0.05 to 2 parts by weight based on 100 parts of said coal tar of a mixed alkali metal base-basic organic amine salt of an interpolymer of from about 95% to 99.99% by weight of acrylic acid and from about 0.01% to about 5% by weight of an olefinic monomer having at least two olefinic groups in each molecule said alkali metal base being selected from the group consisting of alkali metal hydroxides, oxides and carbonates and said organic amine having at least 6 carbon atoms the weight ratio of said base to said amine being from about 0.0125:1 to 0.2:1 respectively said dispersion having a pH of from about 5 to 8.

5. A stable tar-in-water dispersion comprising at least 35 parts by weight of water, up to 65 parts by weight of homogeneously and finely-dispersed RT-1 to 12 coal tar and as the sole emulsifying and dispersing agent from 0.06 to 1.5 parts by weight based on 100 weight parts of said coal tar of a mixed sodium hydroxide-polyethylene oxide modified dodecyl amine salt of an interpolymer of from about 95% to 99.99% by weight of acrylic acid and from about 0.01% to 5% by weight of a polyallyl sucrose the weight ratio of said hydroxide to said amine being from about 0.0125:1 to 0.2:1 respectively said dispersion having a pH of from about 5.2 to 7.

6. A stable tar-in-water dispersion comprising at least 35 parts by weight of water, up to 65 parts by weight of homogeneously and finely-dispersed RT-1 to 12 coal tar and as the sole emulsifying and dispersing agent from 0.06 to 1.5 parts by weight based on the weight of said coal tar of a mixed sodium hydroxide-dodecylamine salt of an interpolymer of from about 95% to 99.99% by weight of acrylic acid and from 0.01% to 5% by weight of a polyallyl sucrose the weight ratio of said hydroxide to said amine being from about 0.0125:1 to 0.2:1 respectively said dispersion having a pH of from about 5.2 to 7.

7. A stable tar-in-water dispersion comprising at least 35 parts by weight of water, up to 65 parts by weight of homogeneously and finely-dispersed RT-1 to 12 coal tar and as the sole emulsifying and dispersing agent from 0.06 to 1.5 parts by weight based on the weight of said coal tar of a mixed sodium hydroxide-polyethylene oxide modified dodecylamine salt of an interpolymer of from about 95% to 99.99% by weight of acrylic acid and from 0.01% to 5% by weight of tetra vinyl silane the weight ratio of said hydroxide to said amine being from about 0.0125:1 to 0.2:1 respectively said dispersion having a pH of about 5.2 to 7.

8. A stable tar-in-water dispersion comprising at least 35 parts by weight of water, up to 65 parts by weight of homogeneously and finely-dispersed RT-1 to 12 coal tar and as the sole emulsifying and dispersing agent from 0.06 to 1.5 parts by weight based on the weight of said coal tar of a mixed sodium hydroxide-polyethylene oxide modified dodecylamine salt of an interpolymer of from about 95% to 99.99% by weight of acrylic acid and

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from 0.01% to 5% by weight of 1,8-nonadiene the weight ratio of said hydroxide to said amine being from about 0.0125:1 to 0.2:1 respectively said dispersion having a pH of about 5.2 to 7.

9. A stable tar-in-water dispersion comprising at least 35 parts by weight of water, up to 65 parts by weight of homogeneously and finely-dispersed RT-1 to 12 coal tar and as the sole emulsifying and dispersing agent from 0.06 to 1.5 parts by weight based on the weight of said coal tar of a mixed sodium hydroxide-polyethylene oxide modified dodecylamine salt of an interpolymer of from about 95% to 99.99% by weight of acrylic acid and from 0.01% to 5% by weight of tetraallyl silane the weight ratio of said hydroxide to said amine being from about 0.0125:1 to 0.2:1 respectively said dispersion having a pH of about 5.2 to 7.

10. A stable tar-in-water dispersion comprising at least 35 parts by weight of water, up to 65 parts by weight of homogeneously and finely-dispersed RT-1 to 12 coal tar and as the sole emulsifying and dispersing agent from 0.06 to 1.5 parts by weight based on the weight of said coal tar of a mixed sodium hydroxide-polyethylene oxide modified dodecyl amine salt of an interpolymer of from about 95% to 99.99% by weight of acrylic acid and from 0.01% to 5% by weight of tetra-allyl pentaerythritol the weight ratio of said hydroxide to said amine being from about 0.0125:1 to 0.2:1 respectively said dispersion having a pH of about 5.2 to 7.

11. The method for preparing stable tar-in-water dispersions comprising stirring in water as the sole emulsi-

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fyng and dispersing agent a carboxyl containing polymer of (1) at least 20% by weight of an alpha, beta-olefinically unsaturated carboxylic acid, (2) up to about 80% by weight of another monoolefinic monomer copolymerizable with (1) and (3) from about 0.01 to about 10% by weight based on the total weight of monomer of an olefinic monomer having at least two polymerizable olefinic groups in each molecule, neutralizing said polymer to a pH of from about 5 to 8 with a mixture of an organic amine having at least 6 carbon atoms and being selected from the class consisting of aliphatic primary, secondary, tertiary amines, quaternary amine hydroxides and alkylene oxide-treated amines and an alkali metal base selected from the group consisting of alkali metal hydroxides, oxides and carbonates, the weight ratio of said base to said amine being from about 0.0125:1 to 0.2:1 respectively and slowly adding a molten RT tar to the stirred polymer-water mixture.

12. The method of claim 11 wherein at least 35 parts by weight of water, up to about 65 parts by weight of coal tar and from about 0.05 to 2 parts by weight of the polymer based on the weight of said coal tar are employed.

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