Patented Sept. 5, 1950

2,521,542

UNITED STATES PATENT OFFICE

2,521,542

BITUMINOUS EMULSIONS

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No Drawing. Application March 20, 1947, Serial No. 736,111

7 Claims. (Cl. 252—311.5)

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This invention relates to aqueous emulsions of bituminous substances, such as asphalts, pitches, waxes and the like, and more particularly to emulsions of such substances made by the use of water swellable clays such as bentonite, as the emulsifying agent.

Bituminous emulsions of the type above referred to are well known and have been employed for various industrial purposes. These emulsions, as normally manufactured, are composed, for example, in the case of asphalt emulsions, of from approximately 45 to 60% of asphalt, 2 to 3% of bentonite as the emulsifying agent and 38 to 52% of water, depending upon the softening point and other physical properties of the asphalt and upon the technique employed to bring about emulsification thereof. Generally speaking, the asphalt is emulsified by heating the same to a temperature substantially above its softening point and feeding it while in molten state and at a predetermined temperature to suitable emulsifying apparatus, concurrently with the feeding thereto of an aqueous suspension or slip of the bentonite. The emulsifying apparatus is provided with agitating blades of suitable design so that in the operation the liquefied asphalt becomes dispersed or emulsified in the aqueous phase by forces of attenuation and interfacial trituration, the emulsified particles being held in suspension in the aqueous phase and prevented from coalescing therein by the adsorbed films of water and bentonite.

Depending mainly upon the character of the asphalt and the amount of water employed in the manufacture, asphalt emulsions of the type above described are of rather viscous, sometimes pasty, consistency when discharged from the emulsifying apparatus. Since the water is in the external phase, these emulsions can be thinned by dilution with water but this means of reducing the viscosity of the emulsions is undesirable, especially where the emulsions are to be shipped over any considerable distance from the point of their manufacture to the point of their use. It is known that the fluidity of these emulsions may be increased without increasing the water content thereof, by subjecting the emulsion to a beating action, as described, for example, in the patent to Kirschbraun No. 1,616,904. The amount of thinning action that may be effected by such beating treatment is, however, of a limited order. Furthermore, even when thus thinned, these emulsions exhibit a strong tendency to gel during storage and shipment, the thick gelled consistency making it difficult to handle the material at the point of use. Frequently, the emulsions became gelled to an extent such that

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they do not have sufficient fluidity to enable them to be discharged from bung-type drums or other containers in which they are shipped.

The principal object of the invention is to provide emulsions of the general character above indicated, having, however, considerably higher fluidity than is normally characteristic thereof, without materially increasing the water content.

More specifically, it is an object of the invention to provide emulsions of this character, which will retain the higher degree of fluidity over relatively long periods of time during which the product may be in storage or shipment.

In the patent to Kirschbraun No. 1,918,759, it is proposed to convert the relatively thick short-bodied consistency of bituminous emulsions made with bentonite as the emulsifying agent into a relatively thin long-bodied consistency, by treating them with small quantities of certain organic acids. Although certain of the acids referred to in that patent have been found to be effective for that purpose, the viscosity depressing effect thereof in most instances is primarily an initial effect which does not endure for a substantial period of time, the emulsion reverting to a substantially thickened or non-fluid condition within relatively short periods of time, especially when stored in metal containers.

I have found that the viscosity of emulsions of the type here referred to may be lowered to a satisfactory extent and that this depressed viscosity of the emulsion may be maintained without reversion of the emulsion to a non-fluid condition when the emulsion is stored for substantial periods of time, by treating the emulsion with relatively small quantities of water soluble alkaline salts of certain organic acids, as hereinafter to be more particularly set forth, the amount of the salt employed for this purpose being governed largely by the initial viscosity of the emulsion, and the degree and permanence of viscosity depressing effect desired.

More specifically, I have found that the alkaline salts, and preferably the sodium salts, of such acids as tannic acid, gallic acid and pyrogallic acid, when employed in relatively limited amounts, of the order of from 0.05% to 0.5%, by weight of the emulsion, are effective for bringing about a very marked reduction in the viscosity of the emulsion. Moreover, when these salts are employed in suitable proportions, the viscosity of the emulsion will not materially increase over considerable periods of time, say of the order of 30 to 90 days.

In the case of sodium tannate, the amount thereof may vary from 0.06% to 0.2% by weight of the emulsion; with sodium gallate the amount

employed may vary from 0.05% to 0.5% by weight of the emulsion; and when employing sodium pyrogallate, the amount may vary from 0.05% to 0.30% by weight of the emulsion.

Thus by my invention it becomes possible, for example, to produce bituminous emulsions containing as high as 57% to 60% of dispersed bitumen, but having a fluidity comparable to or higher than that of an emulsion containing 45% to 58% of the same bitumen, as normally made without the treatment embodying the invention.

Preferably, the treatment of the emulsion with the selected salt is effected in the presence of a small excess of free alkali, as may be obtained by reacting sodium hydroxide with the corresponding organic acid in an amount in excess of that required to react with all the available carboxyl and hydroxyl groups of the acid. I have found that the provision of such excess alkali inhibits progressive gelation and consequent thickening of the emulsion which might otherwise result from electrolytic action when the emulsion is stored or shipped in metal containers. The amount of excess alkali for this purpose is such as to impart to the treated emulsion a pH value within the range of approximately 7.8 to 12.0.

In terms of actual measurement, the fluidity of the emulsions herein referred to is reflected by the readings in centipoises taken on a Brookfield viscosimeter at temperatures of 77–85° F. From the practical standpoint, the emulsions are considered to possess a fluidity satisfactory for handling if Brookfield viscosity value thereof is less than about 7000 centipoises. Preferably, however, the viscosity should not exceed 4500 centipoises. These values are the average of the centipoise readings taken with the spindle of the Brookfield viscosimeter rotating at speeds of 6, 12, 30 and 60 R. P. M., and when the readings have come to equilibrium (usually after about five minutes).

In referring to the fact that the emulsions produced in accordance with the invention do not undergo material increase of viscosity during storage for a stated period of time, it is meant that the viscosity at the end of the period of storage will nevertheless be within the range of values above indicated, though the viscosity may be higher than when measured at the beginning of the storage period. In this sense, the fluidity of the emulsion may be considered as virtually unchanged, for although the numerical rise in centipoise viscosity reading may be higher at the end of the storage period than at its beginning, the product is as fluid for handling after the storage period as at its outset. In other instances, the viscosity at the end of the storage period may be even lower than at the outset.

The treatment of the emulsion according to the invention is preferably performed by incorporating the selected treating salt in the emulsion when the latter is at a substantially lower temperature than that at which it is discharged from the emulsifying apparatus. The temperature of the emulsion at the time of treatment may be from normal atmospheric to about 135° F.

Preferably, the required amount of the selected salt is added to the emulsion in the form of a concentrated solution thereof in water, usually not less than a 10% solution, in order that the amount of additional water thereby added to the emulsion shall be as little as possible. The solution of the salt is preferably incorporated in the emulsion in successive increments while the

emulsion is stirred or agitated, although in certain instances it may be desirable to incorporate a portion of the solution, constituting in some cases only a minor portion thereof, in the manner above indicated, the balance being added to the thus treated emulsion after it has been delivered to a storage tank.

The following are specific examples, illustrating the practice of the invention:

Example I

This example illustrates the invention as applied for the treatment of an emulsion of asphalt of relatively high softening point asphalt, say 175 to 185° F., and having relatively high solids content (i. e., relatively low water content). Asphalt having a softening point of approximately 185° F., and 0 penetration (at 77° F.), is emulsified in water, with bentonite clay as the emulsifying agent. The emulsification is carried on so as to produce a base emulsion having substantially the following composition, in parts by weight:

Asphalt	54.5
Bentonite	2.5
Water	43

As normally produced, this emulsion is of a heavy paste consistency (far too heavy to permit of taking a viscosity reading on the Brookfield, the maximum reading on which is 100,000 centipoises) and its pH value is approximately 6.5.

In 99.8 parts of the above emulsion there is incorporated 0.2 part of sodium tannate (solids, by weight, based on the total emulsion) composed of equal parts by weight (solid basis) of sodium hydroxide and tannic acid in a 10% aqueous solution. This solution is added to the emulsion in successive increments, the emulsion being preferably agitated during the addition of at least the first several increments of the treating solution. By this treatment, although the water content has been increased only to approximately 43.6% from the original water content of 43.0%, the heavy paste or buttery consistency of the base emulsion is transformed to a fluidity of the order reflected by a viscosity of approrimately 1820 centipoises. After a storage period of fifty days, the emulsion thus treated retained its fluidity, exhibiting, if any change in this respect, a thinner consistency than at the beginning of the storage period, as reflected by a viscosity of the order of 860 centipoises.

It will be noted that in this example, sodium tannate was made up of equal parts by weight of sodium hydroxide and tannnic acid. Tannic acid having a molecular weight of 322.2 and sodium hydroxide having a molecular weight of 40, it will be seen that equal parts by weight is equivalent to 8 moles of sodium hydroxide to 1 mole of tannic acid, or an excess of 2 moles of sodium hydroxide over the alkali required to react with all the available (six) hydroxyl groups of the tannic acid. In terms of excess alkali, this amounts to 0.026% free alkali, based on the total weight of the emulsion, resulting in a pH value of 11.6.

Example II

In this example, a similar base emulsion as referred to in Example I is treated with the same quantity of sodium tannate as in Example I, but in this instance the sodium tannate was made up of 1 part of tannic acid and 0.75 part of sodium hydroxide (solids weight basis), in solution in 2 parts water. It will be seen, therefore, that in this example, the sodium tannate is made up

of one mole of the acid and six moles of the alkali, i. e., the amount of alkali used was the amount required to react with all the available (six) hydroxyl groups of the tannic acid, and no free alkali was, therefore, present. The thus treated emulsion had a pH of 8.9.

The result of this treatment upon the base emulsion was to transform its initial heavy paste consistency into a fluid condition of the order indicated by a viscosity of approximately 19,000 centipoises. Although the viscosity depressing effect was thus less than in the treatment in accordance with Example I, the treated emulsion of this example exhibited a sufficient thinning out trend, so that at the end of a storage period of approximately seventy days, the viscosity was approximately 4300 centipoises. From a practical point of view, the emulsion thus treated is fluid enough to be discharged from a bung-type drum, though not as fluid as is usually desirable for shipment in this type of container.

Example III

In this example, 99.8 parts, by weight, of the same base emulsion as referred to in Example II, is treated with 0.2 part (by weight solids based on the total emulsion) of sodium tannate composed of 3 parts of sodium hydroxide (solid basis) and 1 part tannic acid (solid basis), in a 20% aqueous solution. It will be noted that the sodium tannate used in this example contained 18 moles of excess sodium hydroxide; in terms of free alkali, this amounts to 0.112% free sodium hydroxide by weight, based on the total emulsion. The pH value of the treated emulsion was 11.6. With the sodium tannate of this example, the heavy paste condition of the base emulsion was transformed to a fluid condition reflected by viscosity reading of 1720 centipoises. The fluidity remained substantially unaltered during a storage period of ninety-five days, at which time it exhibited, if any change in this respect, a slight decrease in viscosity, viz., to 1620 centipoises.

Example IV

In this example, the invention is illustrated with reference to an emulsion of an asphalt of substantially the same softening point as that in the previous examples, but the base emulsion as initially produced having a substantially higher water content than the base emulsion of the previous examples.

The base emulsion was made so as to have substantially the following composition, in parts by weight:

Asphalt (softening point 135° F.; penetration at 77° F.)	45.2
Bentonite	2.8
Water	52.0

The emulsion thus produced possesses a fluidity reflected by a viscosity of approximately 17,000 centipoises, and exhibits a tendency to gel to somewhat non-fluid condition in storage.

99.94% parts by weight of the emulsion was treated with 0.06 part by weight of sodium tannate made up of equal parts by weight (solid basis) of tannic acid and sodium hydroxide. This is equivalent, as in the case of Example I, to a ratio of 1 mole tannic acid to 8 moles sodium hydroxide. The sodium tannate was employed in a 20% aqueous solution. This treatment resulted in a sizeable initial reduction in viscosity (to approximately 2000 centipoises) with a slight trend to thinning out during storage, so that at the end of a period of twenty-two days storage, the viscosity of the emulsion was approximately 1450 centipoises.

Example V

In this instance, the treatment in accordance with the invention was applied to an emulsion of an asphalt having a softening point of 110 to 120° F., i. e., a considerably lower softening point than that referred to in the previous examples, the emulsion, however, having a water content approximately the same as the base emulsions in Example I, II and III.

Steam refined asphalt having a softening point of approximately 112° F., and a penetration of 85 to 100 at 77° F., is emulsified with bentonite as the emulsifying agent, to produce a base emulsion having substantially the following composition, in parts by weight:

Asphalt	57.0
Bentonite	2.0
Water	41.0

This base emulsion has a pH value of approximately 7.2 and a fluidity such as reflected by a viscosity of 23,000 centipoises. 99.9 parts by weight of this base emulsion was treated with 0.1 part by weight of sodium tannate composed of 1 part tannic acid and 0.75 part sodium hydroxide (solids basis). In other words, the sodium tannate was made up of one mole of the tannic acid and six moles of sodium hydroxide. The pH of the treated emulsion was 9.5. The effect of this treatment was to depress the viscosity to a value of approximately 3500 centipoises, this viscosity remaining substantially unaltered during a storage period of thirty-two days.

Example VI

99.94 parts by weight of the same base emulsion as referred to in Example V, was treated with 0.06 part by weight of sodium tannate composed of equal parts by weight of sodium hydroxide and tannic acid. Thus, in this instance, the sodium tannate was made up in a molar ratio of 3 moles of sodium hydroxide to 1 mole of tannic acid, or an excess of 2 moles of sodium hydroxide over the alkali needed to react with the available hydroxyl groups.

Under these conditions, the treatment of the emulsion with the sodium tannate depressed the viscosity of the emulsion to substantially the same extent, namely, to a viscosity of about 3500 centipoises, as in the case of the sodium tannate employed in Example V. However, whereas in the case of Example V there was no material change of viscosity after a storage period of thirty-two days, the viscosity of the emulsion treated according to this example increased somewhat, viz., to approximately 6700 centipoises, when stored for thirty-two days. From this standpoint, therefore, the treatment according to Example V may be considered as providing a better over-all effect for this base emulsion than does the treatment of this example.

Example VII

99.85 parts by weight of the same base emulsion as referred to in Example V was treated with 0.15 part by weight of sodium gallate made by reacting sodium hydroxide with gallic acid in proportions to provide a mole ratio of 1 mole of the acid to 4 moles of the hydroxide. The treated emulsion had a pH value of 9.5. This treatment resulted in depressing the viscosity of the base

emulsion to a viscosity of the order of 1200 centipoises. After a thirty-two day storage period, the viscosity increased only slightly. Thus, the treatment according to this example may be considered more effective for this base emulsion than either of the treatments described in Examples V and VI.

Example VIII

In this example, there is illustrated the use of sodium pyrogallate as the viscosity depressing agent.

In this instance, 99.8 parts of a base emulsion of 185° F. melt point asphalt having a water content of 46.0% were treated with 0.2% part by weight of sodium pyrogallate made by reacting sodium hydroxide with pyrogallic acid in proportions to provide a mole ratio of 1 mole of the acid to 3 moles of the hydroxide. This treatment resulted in depressing the viscosity of the base emulsion from a paste consistency to approximately 1100 centipoises. The pH of this emulsion was 10.1.

Example IX

In this example, there is illustrated the use of sodium gallate as the viscosity depressant.

In this instance 99.94 parts of a base emulsion of 185° F. melt point asphalt having a water content of 50.0% were treated with 0.06 part by weight of sodium gallate, made by reacting 1 mole gallic acid with 4 moles sodium hydroxide. (The base emulsion had been stored for a considerable time and in spite of the high water content had gelled to paste consistency.) The treatment resulted in depressing the viscosity from a paste consistency to approximately 1200 centipoises. The pH of this emulsion was 7.8.

I claim:

1. A bituminous emulsion consisting essentially of approximately 45 to 60% bitumen as the disperse phase, approximately 1.5 to 3% bentonite as the emulsifying agent and water as the continuous phase, and containing approximately 0.05 to 0.5% by weight of an alkali metal salt of an organic acid selected from the group consisting of tannic acid, gallic acid and pyrogallic acid, the amount of said salt being sufficient to impart to the emulsion a viscosity substantially lower than it normally possesses in the absence of said salt.

2. A bituminous emulsion consisting essentially of approximately 45 to 60% bitumen as the disperse phase, approximately 1.5 to 3% bentonite as the emulsifying agent and water as the continuous phase, and containing approximately 0.05 to 0.5% by weight of an alkali metal salt of an organic acid selected from the group consisting of tannic acid, gallic acid and pyrogallic acid, the amount of said salt being sufficient to impart to the emulsion a viscosity substantially lower than it normally possesses in the absence of said salt, and an amount of free alkali to impart to the emulsion a pH value within the range of 7.3 to 12.0.

3. A bituminous emulsion consisting essentially of approximately 45 to 60% of bitumen as the disperse phase, approximately 1.5 to 3% bentonite as the emulsifying agent and water as the continuous phase, and containing approximately 0.05 to 0.5% by weight of an alkali metal salt of an organic acid selected from the group consisting of tannic acid, gallic acid and pyrogallic acid, said emulsion being characterized by an initial viscosity and a viscosity after storage for a period of not less than 20 days, substantially lower than the initial viscosity and the viscosity after such storage period, of said emulsion in the absence of said salt.

4. A bituminous emulsion consisting essentially of approximately 45 to 60% bitumen as the disperse phase, approximately 1.5 to 3% bentonite as the emulsifying agent and water as the continuous phase, and containing 0.06% to 0.2% of sodium tannate, said emulsion being characterized by an initial viscosity and a viscosity after storage for a period of not less than 20 days, substantially lower than the initial viscosity and the viscosity after such storage period, of said emulsion in the absence of said sodium tannate.

5. A bituminous emulsion consisting essentially of approximately 45 to 60% of bitumen as the disperse phase, approximately 1.5 to 3% bentonite as the emulsifying agent and water as the continuous phase, said bitumen having a softening point of approximately 175 to 185° F., said emulsion containing 0.06 to 0.2% by weight of sodium tannate, said emulsion being characterized by an initial viscosity and a viscosity after storage for a period of not less than 20 days, substantially lower than the initial viscosity and the viscosity after such storage period, of said emulsion in the absence of said sodium tannate.

6. A bituminous emulsion consisting essentially of approximately 45 to 60% of bitumen as the disperse phase, approximately 1.5 to 3% bentonite as the emulsifying agent and water as the continuous phase, said bitumen having a softening point of approximately 110 to 120° F., said emulsion containing 0.05 to 0.5% by weight of sodium gallate, said emulsion being characterized by an initial viscosity and a viscosity after storage for a period of not less than 20 days, substantially lower than the initial viscosity and the viscosity after such storage period, of said emulsion in the absence of said sodium gallate.

7. A bituminous emulsion consisting essentially of approximately 45 to 60% of bitumen as the disperse phase, approximately 1.5 to 3% of bentonite as the emulsifying agent and water as the continuous phase, and containing 0.05 to 0.3% by weight of sodium pyrogallate, said emulsion being characterized by an initial viscosity and a viscosity after storage for a period of not less than 20 days, substantially lower than the initial viscosity and the viscosity after such storage period, of said emulsion in the absence of said sodium pyrogallate.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,918,759	Kirschbraun	July 18, 1933
1,963,231	Fain	June 19, 1934
1,995,346	Halvorsen	Mar. 26, 1935
2,380,156	Dobson	July 10, 1945

FOREIGN PATENTS

Number	Country	Date
246,907	Great Britain	Feb. 3, 1926
350,744	Great Britain	June 18, 1931

OTHER REFERENCES

Role of Clay and Other Minerals in Oil Well Drilling Fluids. Report of Investigation by Bureau of Mines. Feb. 1941, R. I. 3556, p. 68. (Copy in Division 64.)