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SEARCH ROOM

Oct. 31, 1961 H. J. SOMMER ET AL 3,006,354

METHOD FOR TRANSPORTING LIQUIDS THROUGH PIPELINES

Filed March 15, 1956 2 Sheets-Sheet 1

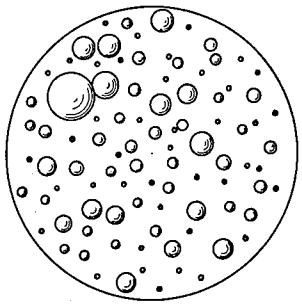

FIG. I

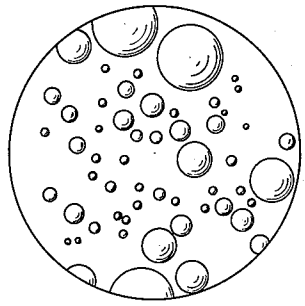

FIG. II

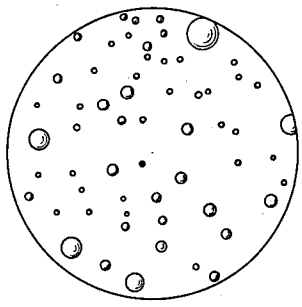

FIG. III

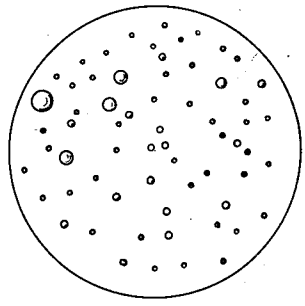

FIG. IV

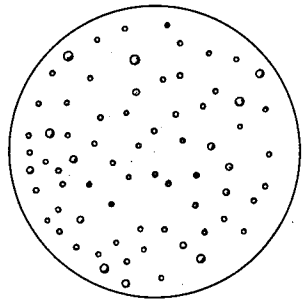

FIG. V

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THEIR AGENT

METHOD FOR TRANSPORTING LIQUIDS THROUGH PIPELINES

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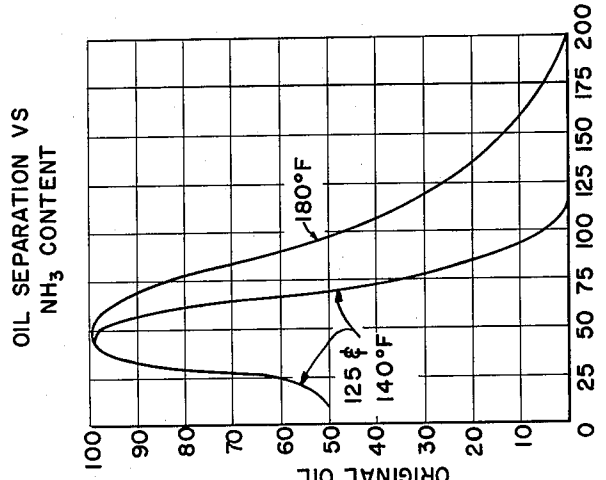

FIG. VIII

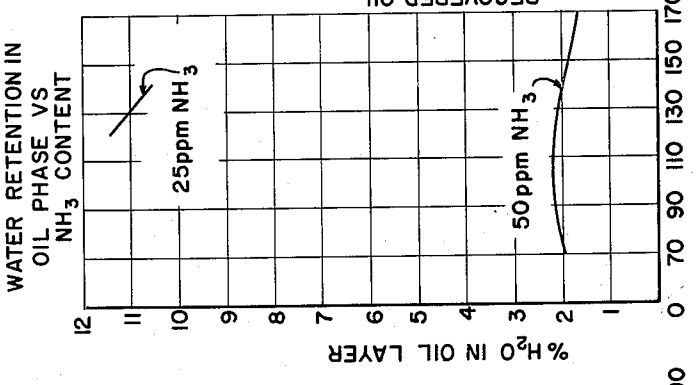

FIG. VII

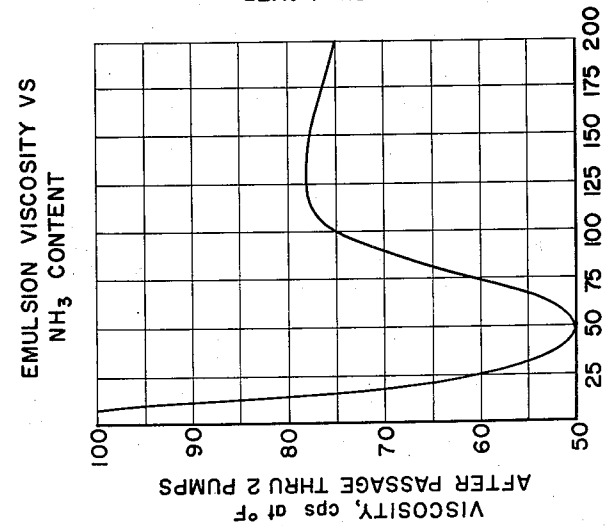

FIG. VI

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3,006,354

METHOD FOR TRANSPORTING LIQUIDS THROUGH PIPELINES

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1 Claim. (Cl. 137—13)

This invention relates to a method for increasing the throughput capacity of pipelines used for transporting viscous oils and the like.

The transportation of extremely viscous oils such as crude mineral oil, coal tars, vegetable oils and petroleum products through pipelines presents difficulty, especially during cold weather. Even when pressures near the maximum permissible for standard pipe and pumping equipment are employed, such oils may be so viscous that special procedures are required to make pipeline transportation practical.

It has been customary to facilitate the flow of very heavy crude petroleum and the like by reducing its viscosity either through the addition of a hydrocarbon diluent or through the installation of heating equipment at suitably spaced stations along the pipeline. The former expedient is practicable only in the somewhat unusual case where a supply of light petroleum product is available in the same region from which the heavy petroleum is taken, and the latter expedient is inconvenient and costly.

It is known that substantial amounts of water may be introduced into a pipeline containing a stream of viscous petroleum flowing therethrough to reduce the drag on the stream and thus facilitate the flow through the pipeline. This has been done by the incorporation of water together with oil in the pipe such that an "enveloping" action of the water occurs without violent enough shearing to cause the formation of water-in-oil emulsions. This, of course, limits the throughput of the line to those conditions under which laminar flow exists. Under the well-known conditions for emulsification, on the other hand, such stable emulsions may form, causing difficulty at the terminal of the line when separation of the oil and water is desired. Under these circumstances, uneconomical amounts of demulsifying agents have been required. Likewise, methods are known for the reduction in water content such as disclosed in the Clark patent, U.S. 2,533,878, wherein from 7 to 15% of water is employed, the water being modified by the presence of a water-soluble anionic surface-active agent, an alkali metal phosphate and the pH adjusted to within the range 5.7 to 7.0. As the data contained in this patent show, it is necessary to maintain the operation of a system such as this under laminar flow conditions (as opposed to turbulent flow conditions). This process likewise seriously limits the throughout rate of oil.

An improvement on this method is described in the copending Chilton et al. U.S. application, Serial No. 318,004, filed October 31, 1952, wherein amounts of water in the order of 1% are introduced into the stream of viscous petroleum under such circumstances that the water wets the sides of the pipe and thus reduces the friction which normally occurs between pipe walls and the body of viscous liquid passing therethrough. However, this method likewise is dependent upon the formation and maintenance of a water film on the inner surface of the pipe. Once the water film has been destroyed, the viscosity advantage disappears. The method is most useful for short lengths of pipe and especially where laminar flow conditions are practical.

Due to the fact that pipelines are relatively expensive installations, it is an economic necessity in most cases to operate them under high throughput conditions, if it

is at all possible to do so. However, it is substantially impossible to employ the methods described above for the transportation of viscous oils at high oil throughput rates. Since stable water-in-oil emulsion difficulties are usually encountered, the alternative course, namely, the heating of the pipeline and the use of diluents which must be removed at the terminus, are undesirable expedients to be avoided if possible.

Our copending U.S. patent application Serial No. 462,879, filed October 18, 1954, now abandoned, describes an improved process for the transportation of viscous oils comprising the incorporation of a critically limited amount of water with the crude oil and transporting the mixture, wherein at least the water is under turbulent flow conditions, through the pipeline. When the amount of water is limited to between about 25 and 45% by weight, based on the total weight of oil and water, minimum horsepower for pumping a given type and quantity of oil is required. While these conditions are satisfactory for the transportation of crude oils and the like in the presence of certain produced waters, especially those having a low mineral content or a low degree of hardness, a certain degree of inversion of the emulsion to form the undesirable water-in-oil type of emulsion may occur. It is highly desirable to maintain the original oil-in-water type of emusion but at the same time to adjust the constituents of the emulsion such that the oil and water phases separate rapidly at the terminal of the pipeline.

It is an object of the present invention to improve the transportation of crude oils and similar viscous water-insoluble liquid products. It is another object of this invention to facilitate the movement through pipelines and similar equipment of viscous petroleum and fractions thereof. It is a further object of this invention to provide a method for moving highly viscous oils through pipelines at a high rate of speed. It is a further object of this invention to provide for the formation of rapid settling emulsions having minimum viscosity during transportation through a pipeline.

In the description of the invention, reference will be made to the following figures:

FIG. I—Emulsion containing no ammonia;

FIG. II—Emulsion containing 50 p.p.m. ammonia based on oil;

FIG. III—Emulsion containing 100 p.p.m. ammonia based on oil;

FIG. IV—Emulsion containing 250 p.p.m. ammonia based on oil;

FIG. V—Emulsion containing 500 p.p.m. ammonia based on oil;

FIG. VI—Plot of emulsion viscosity vs. ammonia content;

FIG. VII—Plot of water retention in oil phase vs. ammonia content;

FIG. VIII—Plot of oil separation vs. ammonia content.

Now, in accordance with this invention, it has been found that emulsions having minimum viscosity, capable of breaking with great rapidity upon standing, and requiring a minimum of power to transport them through a pipeline under either laminar or turbulent flow conditions are produced not only by maintaining a critically limited proportion of water of between about 25 and 45% by weight of the mixture of oil and water, but also of incorporating therein between about 35 and 100 parts per million of ammonia, based on the weight of the oil.

Also in accordance with this invention, it has been found that upon restricting the water and ammonia contents of the oil and water emulsion to within the ranges stated above, the inversion of the emulsion to the undesired water-in-oil type does not occur under operating conditions, at least to any appreciable extent. More-

over, when utilizing ammonia as the emulsifying agent within the concentration ranges recited above, it has been found to be unnecessary to employ demulsifying agents in order to separate the oil and water from each other at the terminal of the line.

Another feature of this invention comprises the modification of the consignment of oil being sent through a pipeline when the pipeline is utilized for the transportation of a multiplicity of crude oils or other oily products. It has been found that when a pipeline is first utilized for the transportation of a relatively lighter petroleum oil followed by an emulsion of a heavier petroleum oil and the water content of the emulsion is maintained between about 25 and about 45%, based on the oil and water content, that an extremely high viscosity frontal zone may be established and builds up where this emulsion contacts residual amounts of the lighter preceding product. In accordance with one phase of the present invention, a means has been found for overcoming this difficulty. In order to minimize frontal zone viscosity build-up and thereby minimize pipe pressures required to transport an emulsion through a pipeline at a given rate of flow, when said emulsion is preceded by a relatively lighter petroleum oil, it is highly desirable to separate or partition the lighter preceding product from the following oil-and-water emulsion by a more dilute emulsion formed between a relatively heavier petroleum oil and between about 48% and 65% by weight of water, based on the total of water and oil. Under these conditions, especially when the length of the intermediate emulsion is an amount between about 25 and about 35 barrels per square inch of cross sectional area of the pipe (for relatively large pipes), the viscosity build-up is minimized and no difficulty is encountered in transporting the succeeding more concentrated emulsions of oil, water and ammonia. The preferred minimum length of intermediate emulsion will increase with the cross section of the pipe from about 50 feet for a one-inch pipe to about one mile in a 12-inch (diameter) line.

In the course of developing the present invention, it was considered that a high throughput would be desirable and that the use of heat or solvents is costly. Moreover, it was realized that by the prior art methods previously discussed, wherein laminar flow conditions were necessary in order to utilize the smallest amounts of water, the capacity of the pipeline was thereby seriously limited. Consequently, it was an aim of the investigation to discover a means for maintaining a high throughput rate without encountering these shortcomings or limitations. However, the limitations on water and ammonia concentration which form the basis of the present invention have been found to apply to laminar flow conditions as well as to turbulent flow.

In the use of high throughput, of course, turbulent flow conditions usually exist, at least in the water phase. Under such conditions, water films on the pipe surface are impossible to establish or maintain. Furthermore, based upon a number of variables such as the viscosity and temperature of the petroleum product and the composition of the water phase as well as upon the rate of throughput, water added to the crude oil or produced therewith from the ground formation may eventually be emulsified within the oil to form water-in-oil emulsions.

It was found that in the absence of water as a continuous phase, compositions comprising petroleum products containing water in the form of water-in-oil emulsions were highly undesirable since the viscosity thereof was ordinarily higher than that of the unmodified petroleum product. Since the principal aim of the entire investigation was to reduce the resistance to flow of the petroleum product through the pipeline, other means were investigated. The possibility existed of utilizing a wide variety of proportions of water to petroleum product. Moreover, the possibility existed of modifying the water, such as was done in accordance with the disclosure of the Clark patent referred to hereinbefore.

A further modification of the water was made and was tested wherein emulsifying agents capable of forming relatively stable emulsions were utilized. It was found that the use of excessive amounts of surface-active agents (and particularly emulsifying agents) was undesirable due to the fact that long residence times were required for the separation of the mixture at the terminal of the pipeline into the aqueous and petroleum phases. Hence, even though the emulsion techniques may be employed, this necessitated either slow throughput rates for unstable suspensions or excessively large residence tanks at the terminal of the lines as well as the expense of emulsion breakers and emulsifying agents when highly stable emulsions were used.

In the study of emulsifying agents, it was found that oil-in-water emulsions satisfactory for the transportation of viscous petroleum products and crude oils were formed by the use of ammonia as the emulsifying agent. However, in a number of cases such emulsions were too stable to be satisfactory and required special procedures at the terminal in order to resolve the emulsion into its separate phases.

It was evident, therefore, that the requirements of the present process, namely, the production of emulsions for the transportation of crude oils and the like, differed largely from those present in the formation of asphalt emulsions wherein emulsifying agents and, more particularly, ammonia, have been employed. It is elementary in the formation of normal asphalt emulsions that they should be very stable in order to maintain their emulsified state even during long storage periods. This is made possible by the use of higher concentrations of emulsifiers and higher interfacial surface areas. This results in emulsions wherein the particle size of asphalt is as fine as possible and this is promoted furthermore by the passage of the emulsion ingredients together through colloid mills or other high shearing devices.

Contrasted to these desirable features of a normal asphalt emulsion, the emulsions required for the transportation of oil through a pipeline should be sufficiently unstable to separate on standing during a relatively short quiescent period. Hence, it was found that far lower amounts of emulsifying agent were to be desired and relatively low amounts of shear (such as pipe friction and the usual pipeline pumps) should be used so as to maintain the interfacial area at a minimum, no special shearing devices, such as a colloid mill, being required. Under such conditions it was found that the particle size of the oil suspended in water was as coarse as possible and furthermore, of equal importance, a wide distribution in particle size occurred, thus enabling maximum "packing" of drops of oil in a given volume of oil and water. Under the dual conditions specified, namely, the use of 25–45% of water, based on the mixture, and of 35–100 parts per million of ammonia, based on oil, were the ultimate objectives of wide distribution of particle size, coarse particle average and sufficient instability achieved. Further proof of these results will be found in the examples appearing hereinafter.

Although the present invention may be used under either laminar or turbulent flow conditions, it is one of the principal objects of the present invention to enable the transportation by means of pipeline of a maximum quantity of water-insoluble oils during a given period of operation in the absence of heating or solvent dilution. This may result in the use of turbulent flow conditions in the line as opposed to laminar flow which results from lower rates of flow. As the throughput rate is increased, the ratio of water to oil or other petroleum product becomes increasingly critical. This critical character of the proportion of water is with respect to the "suspending" water (i.e. the (external) continuous phase) as contrasted to emulsified water, the latter being regarded for the present purpose as water which has been converted into a water-in-oil type of emulsion. By "suspending" water

is meant water mixed with the petroleum product in such a way that it surrounds the oil as the continuous phase, to form an oil-in-water emulsion. Under the present conditions and in the presence of the defined ratios of ammonia, the water separates readily from the oil whenever the mixture of water and oil is conducted to a storage tank or the like.

It was found that if too little water of the suspending type was present in the petroleum-water mixture, the mixture assumed viscosity characteristics approximating those of the dehydrated petroleum product.

As contrasted to this, it was found that within the critically defined range of suspending water a sharp reduction in horsepower requirement occurred, and, that this requirement became increasingly advantageous as the throughput rate was increased. The most favorable results were obtained when the proportion of suspendnig water was between about 25% and about 45% by weight of the total water-petroleum mixture. It will be understood that this critical range is meant to define the proportion of suspending water and does not include the proportion of emulsified water which may be present.

Under even the most favorable conditions, it is found that a certain amount of water will be retained in the emulsified state with petroleum regardless of whether emulsifying agents are present or absent. This is noted particularly at the terminal of a pipeline when water and oil are being pumped together. It is desirable to separate the maximum amount of water from the petroleum material so as to minimize dehydration requirements or the deleterious effects of water upon refining or other equipment in which the petroleum product is utilized or processed.

As the oil and water proceed through the pipeline under turbulent conditions, there is the possibility that at least part of the water may become emulsified with the oil to form undesired water-in-oil type of emulsions. Since such emulsions exhibit a viscosity similar to or greater than that of the viscous oil, the original benefit of the suspending water will become balanced by the increase in viscosity of the mixture and by the decrease in the proportion of suspending water. This problem is accentuated in direct ratio to the length of the pipe and to the number of pumps through which the mixture passes. Both of these conditions increase the extent of mixing of the two phases and create the conditions favorable for water-in-oil emulsion propagation.

In accordance with one phase of the present invention, the disadvantages of these phenomena may be largely overcome by intermittent injection of water at points throughout the length of line through which the mixture is traveling. The proportion of injection and the number of points of injection cannot be stated with any accuracy since they will vary with the temperature conditions, the length of the pipe, the rate of throughput, the viscosity of the mixture, the number of pumps through which the mixture passes, the chemical constitution of the aqueous phase and the presence or absence of surface-active agents (naturally occurring or otherwise) in either phase. However, the addition of water under such conditions as to maintain the correct proportion of the suspending form thereof in the oil-water mixture promotes the formation of the desired low-viscosity aqueous petroleum mixtures. Preferably, these water injections are made on the downstream side of any pump installation so that the water has the minimum chance of being emulsified within the petroleum oil by the action of the pump.

Not only is it preferred to add supplementary quantities of water on the downstream side of the pump when required for maintenance of low viscosity of the aqueous petroleum mixture, but it is also a preferred (although not essential) practice to inject the original proportion of water to be mixed with the oil in such a way that simultaneous passage of water and oil through the pump at the entrance end of the pipeline is minimized or avoided. Thus, one process comprises separately introducing oil and water into the pipe system, the pressure in the system being applied by separate pumping of both water and oil, and the two components being passed through a length of pipe of such diameter that the desired suspension is created (i.e. a suspension capable of ready settling) without the formation of the undesired water-in-oil emulsions. Under these conditions the formation of the latter will be minimized and the maximum beneficial results of the present invention will be realized.

Under the ideal conditions for the operation of this invention, it is desirable to employ produced water, namely, that water which is produced from the oil well together with the oil. It will be understood that the proportion of produced water will vary widely from one well to another even within a restricted portion of the same oil field. The proportion of produced water even varies from time to time in the wet oil produced from any given well. It therefore appears to be desirable to carry the wet oil to a storage tank wherein the oil is separated from as large a proportion of water as possible in a reasonable storage period. This is desirable furthermore so that accurate gauging of the water to be added, for the formation of suspension, to the petroleum oil may be made. It will be further understood that petroleum oils generally contain greater or lesser amounts of naturally-occurring surface-active material which will control to a certain extent the rate at which the aqueous phase will separate therefrom.

As recited hereinbefore, it has been found that the proportion of ammonia to be utilized in the process of the present invention is sharply critical between about 35 parts and about 100 parts per million, based on the weight of the oil. Below about 35 parts per million of ammonia the oil and water mixtures (especially when the water is soft) rapidly exhibit inversion and the viscosity of the emulsion increases greatly. On the other hand, if the proportion of ammonia is increased beyond about 100 parts per million, the particle size of the dispersed oil becomes increasingly smaller and more uniform and the emulsions are correspondingly more difficult to break at the end of the transportation line.

One of the features of the addition of the critically limited proportion of ammonia is that within the recited range a wide distribution in particle size of the dispersed oil results. Below the lower limit of 35 parts per million and even if with special oils or special waters inversion does not occur, the dispersed oil droplets are relatively uniform in size. Under these circumstances the possibility of "packing" of the droplets within the continuous aqueous phase does not exist and either a larger amount of water is required to make the mixture reasonably fluid or the viscosity of the mixture is unduly high. If, however, the proportion of ammonia is limited to 35–100 parts per million of oil, the particle size distribution of the oil is spread over a wide range as will be seen by photomicrographs to be discussed hereinafter.

The following figures illustrate the advantages gained by use of the present invention. Emulsions were prepared containing 70% of a Venezuelan crude oil and 30% of water having the following constitution:

	P.p.m.		P.p.m.
Ca	24	CO_2	31
Mg	47	SO_4	77
Na	370	Cl	669

The crude used in these tests had the following properties:

Viscosity at—	
77° F—cks	3700
122° F—cks	438
180° F—cks	70
°API gravity	13.1
Acid No., mg. KOH/g	3.2

FIG. I shows the type of emulsion formed when no ammonia is present in the system. It will be noted from the figure that the particle size distribution is relatively narrow, all of the particles being of the same order of magnitude.

FIG. II represents the same emulsion and proportions of ingredients containing in addition 50 parts per million, based on the oil, of ammonia. It will be seen from this figure that a wide distribution in particle size resulted from this addition of ammonia. The very coarse particles are evident at the top and bottom of the figure, while particles of approximately half the maximum diameter and of less than about one-tenth of the maximum diameter are clearly visible throughout the area.

When the ammonia content is increased to 100 parts per million, the particle size distribution is such as shown in FIG. III. It will be seen from this figure that a large number of the biggest drops of oil have been dispersed to form finer droplets and that the wide distribution of particle size is beginning to disappear. This, of course, results in a dispersion which will shortly be too stable for ready separation when the ammonia content is increased to a slightly higher level.

The results of such an increase are shown in FIG. IV wherein the emulsion contained 250 parts per million of ammonia. This figure indicates that the larger particles have all been eliminated and replaced with finely divided particles of extremely small particle size. This emulsion, of course, is of high viscosity and is too stable to settle into its separate phases without the addition of a demulsifying agent.

FIG. V represents the ultimate and undesirable state of the emulsion when an excessive amount of ammonia has been added thereto. This type of emulsion is to be avoided in the practice of the present invention since it will necessitate the addition of large amounts of demulsifying agents in order to separate the water from the oil and, moreover, the viscosity of the mixture will be excessively great.

In addition to illustrating the effect of ammonia content upon particle size, it can be demonstrated that ammonia content has a drastic and direct effect upon the viscosity of the oil-water mixtures, especially under turbulent flow conditions and when subjected to the action of a pump such as must be done during the pumping of the oil and water mixtures through a pipeline of extended length. FIG. VI illustrates this effect with especial clarity. It will be seen by reference to the figure that when amounts of ammonia less than about 35 parts per million were utilized, and the mixtures were subjected to the action of two passes through a gear pump, the emulsion rapidly inverted and the viscosity thereof increased to extremely high figures. A minimum viscosity was attained, as will be seen by FIG. VI, when the ammonia concentration was in the order of about 50 parts per million, based on the oil. As detailed hereinbefore, the special disadvantage of utilizing ammonia concentrations greater than about 100 parts per million comprises the difficulty of separating the oil layer from the water at the terminal of a pipeline.

FIG. VI is based upon emulsions of a Venezuelan crude petroleum oil and water having the analysis given hereinbefore, the mixture containing 70% of oil and 30% of water.

One of the disadvantages of utilizing too little ammonia in the oil and water mixtures, especially when soft waters are employed for this purpose, comprises the water hang-up in the oil layer at the separation stage of the terminal of the transportation process. This is probably due to inversion of part of the emulsion, and the consequent formation of extremely fine particles of water

emulsified with some of the oil to form a water-in-oil emulsion. This feature is illustrated clearly in FIG. VII which shows that if 50 parts per million of ammonia, based on oil, are present in a 30–70 water-oil mixture, less than about 3% water is present in the separated oil phase over a wide temperature range. When, however, only 25 parts per million of ammonia are present in the same mixture of oil and water, the water hang-up in the separated oil phase is in the order of 11% at ordinary separation temperatures.

FIG. VIII shows the result of ammonia content upon the extent of oil separation at three different separating temperatures, namely, 125, 140 and 180° F. Under these circumstances, there is a sharply critical requirement for restricting the ammonia content, especially if lower separation temperatures are utilized. The conditions employed in the construction of FIG. VIII comprised circulation of the mixture of 70 parts of Venezuelan crude oil and 30 parts of soft water, after which the emulsion was allowed to stand in a quiescent state for 2 hours at the indicated temperatures. At the end of that time the amount of separated oil was measured. As will be seen from this figure, it is advisable, at least with this particular crude, to restrict the ammonia content of the emulsion to between about 40 parts per million and about 75 parts per million, unless higher separation temperatures are utilized. Otherwise, longer separation periods will be required.

A California Valley crude, 16° API gravity, was emulsified in water with 50 p.p.m. ammonia to form an emulsion containing 70% crude. This was pumped through a 10- and 12-inch pipeline a distance of about 90 miles with the aid of four pumping stations placed about 22 miles apart at a rate of about 2000 barrels per hour. The average emulsion viscosity was about 50–60 centistokes at 90° F., as compared with 650 centistokes for the crude. At the terminal of the line the emulsion broke readily when heated to about 125° F., no emulsion breaker being necessary. When 100 p.p.m. ammonia were used in a second test, the water-to-crude ratio being the same, it was necessary to heat the mixture at 155° F. at the terminus in the presence of 100 p.p.m. of a commercial emulsion breaker in order to separate the oil and water.

We claim as our invention:

In the pipeline transportation of sequential consignment of a relatively low viscosity crude petroleum oil followed by a dispersion of a relatively high viscosity oil dispersed in water said dispersion having between about 25% and 45% by weight of suspending water, based upon the total weight of high viscosity oil and water and between about 35 and about 100 p.p.m. by weight, based on the high viscosity oil of ammonia, the step comprising forming between the two oils a separating dispersion comprising a relatively high viscosity crude oil dispersed in between about 48% and about 65% by weight of water, based on the weight of oil and water in the separating dispersion, and pumping the low viscosity crude and the two dispersions in sequence through the pipeline.

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