

March 5, 1963

R. J. HOLZINGER ETAL

3,080,322

FIRE-RESISTANT HYDRAULIC FLUIDS

Filed June 8, 1961

6 Sheets-Sheet 1

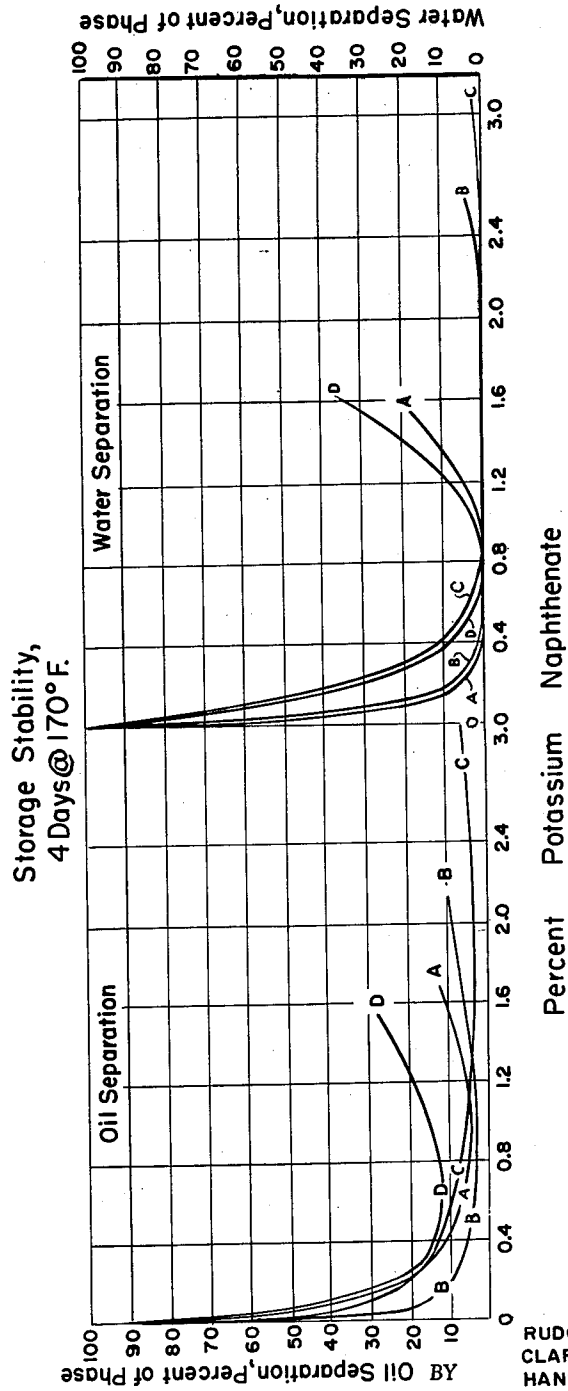


FIG.1

INVENTORS
RUDOLPH J. HOLZINGER,
CLARENCE LIDDY,
HANS F. WALDMAN.

Charles A. Fuggett
ATTORNEY.

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6 Sheets-Sheet 2

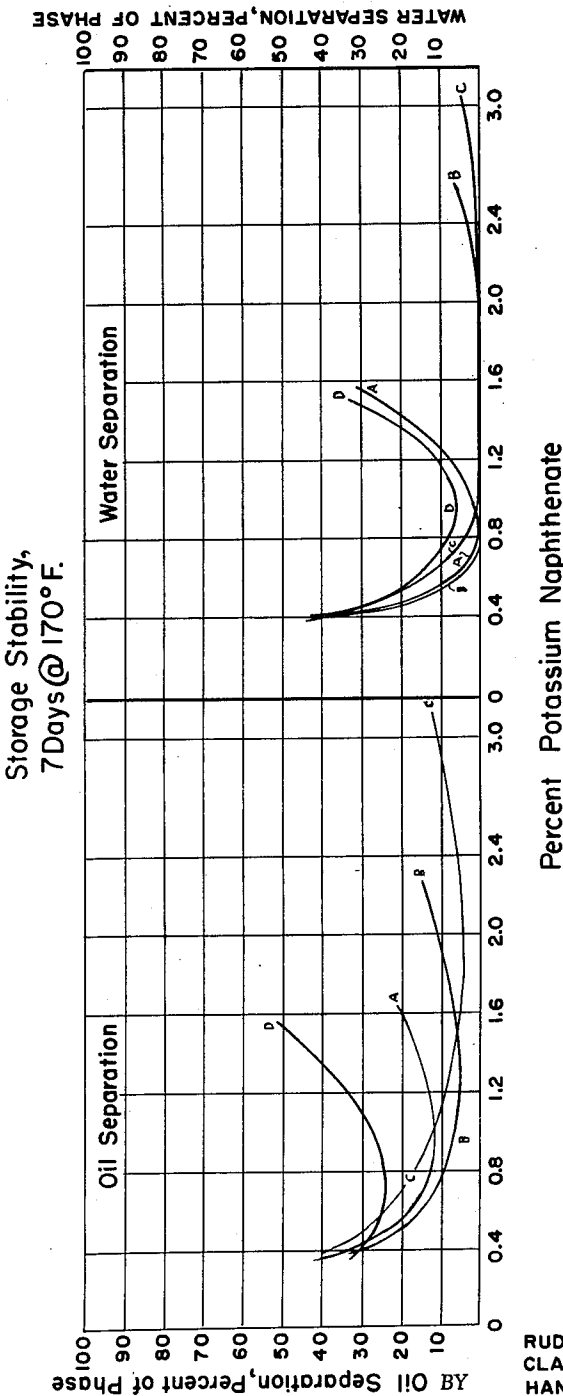


FIG. 2

INVENTORS
RUDOLPH J. HOLZINGER,
CLARENCE LIDDY,
HANS F. WALDMAN.

Charles A. Kugge
ATTORNEY.

March 5, 1963

R. J. HOLZINGER ETAL

3,080,322

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6 Sheets-Sheet 3

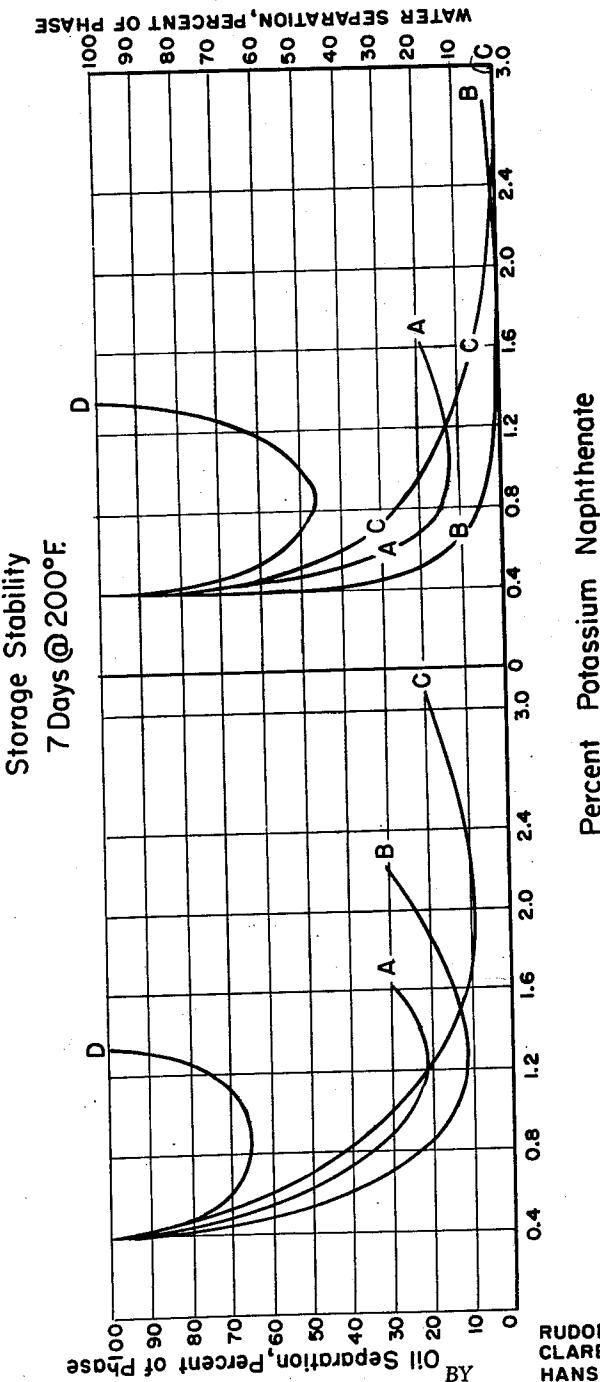


FIG. 3

INVENTORS
RUDOLPH J. HOLZINGER,
CLARENCE LIDDY,
HANS WALDMAN

Charles A. Huggett
ATTORNEY.

March 5, 1963

R. J. HOLZINGER ETAL

3,080,322

FIRE-RESISTANT HYDRAULIC FLUIDS

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6 Sheets-Sheet 4

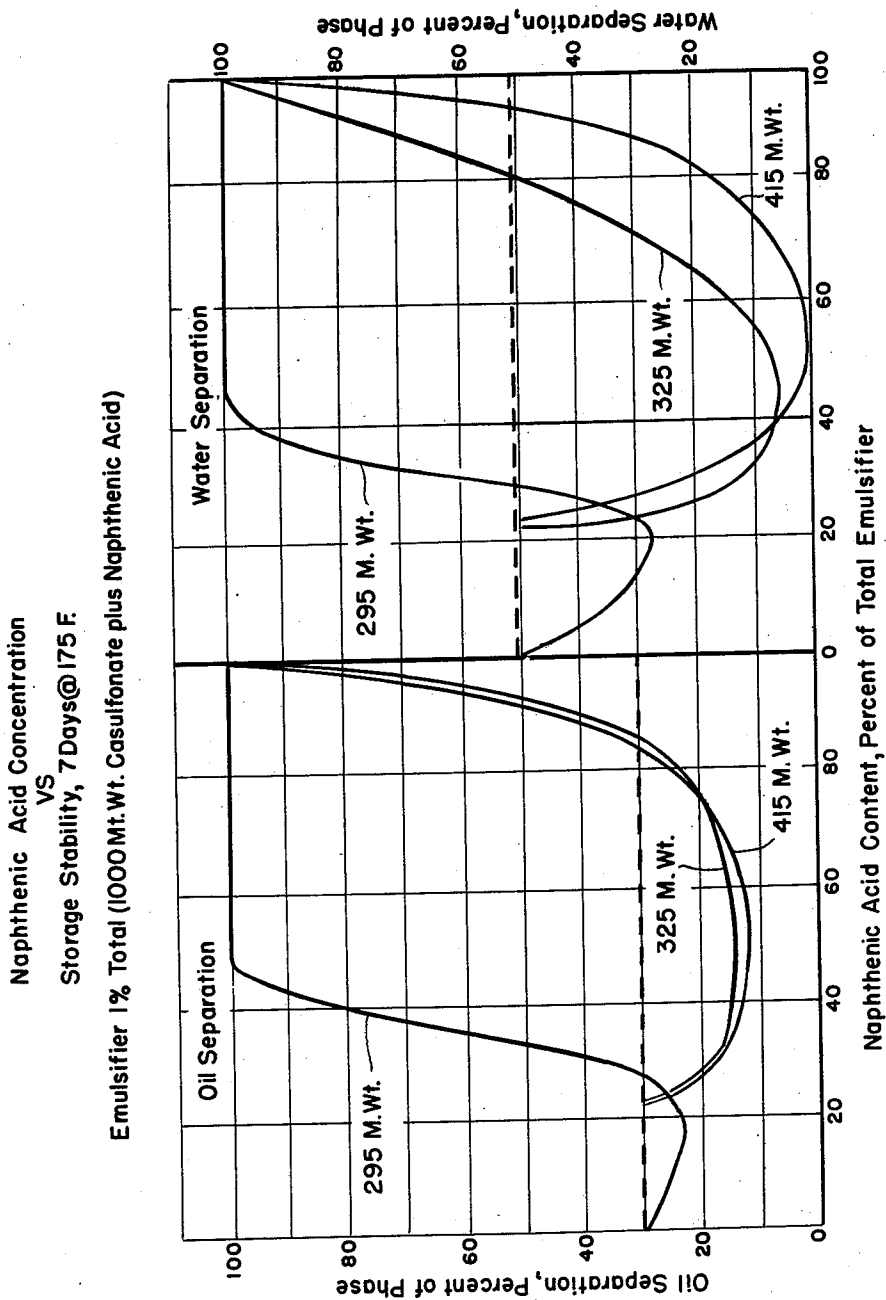


FIG. 4

INVENTORS:
RUDOLPH J. HOLZINGER,
CLARENCE LIDDY,
HANS F. WALDMAN.
BY
Charles A. Fuggett
ATTORNEY.

March 5, 1963

R. J. HOLZINGER ETAL
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6 Sheets-Sheet 5

Storage
1WK@ 200 F., 1WK@ 170 F.,
2WK@ 140 F.

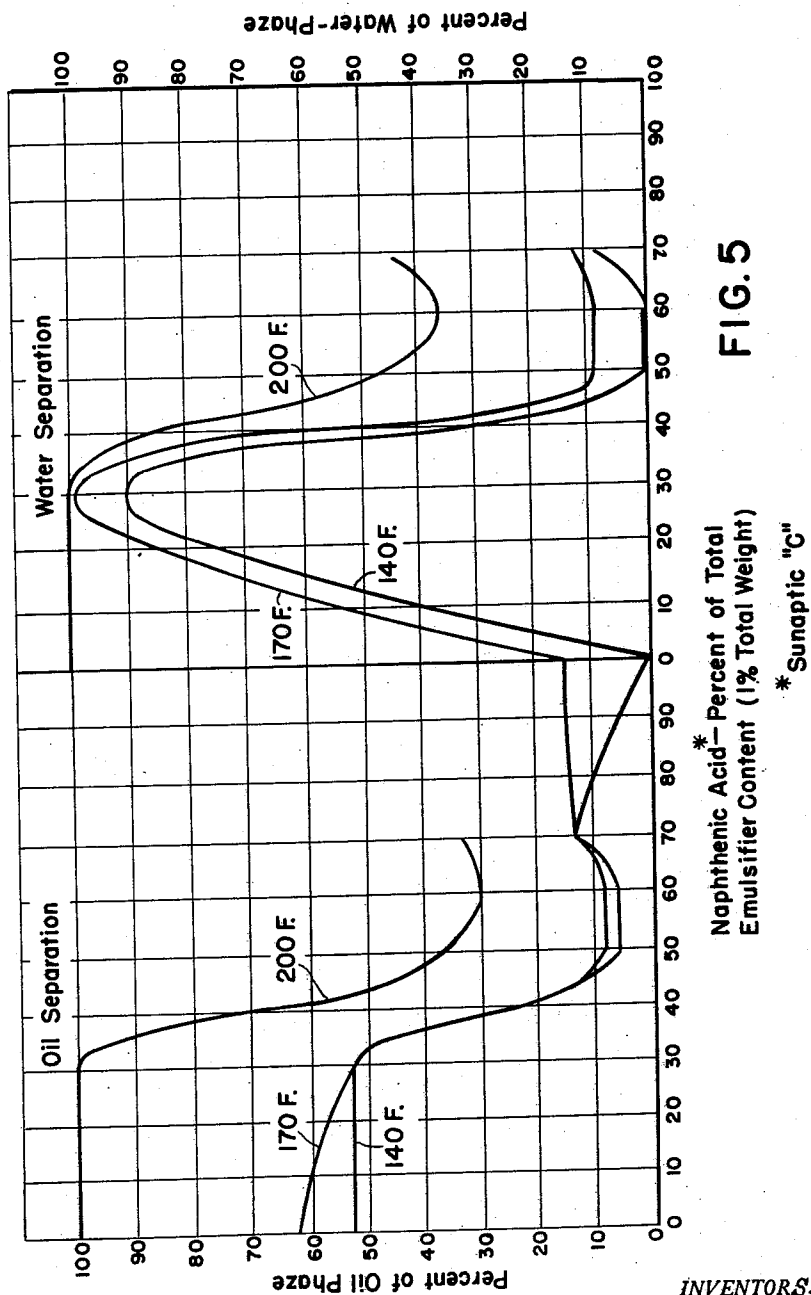


FIG. 5

* Naphthenic Acid - Percent of Total
Emulsifier Content (1% Total Weight)

* Sunaptic "C"

INVENTORS:
RUDOLPH J. HOLZINGER,
CLARENCE LIDDY,
HANS F. WALDMAN.
BY
Charles L. Suggett
ATTORNEY.

March 5, 1963

R. J. HOLZINGER ETAL

3,080,322

FIRE-RESISTANT HYDRAULIC FLUIDS

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6 Sheets-Sheet 6

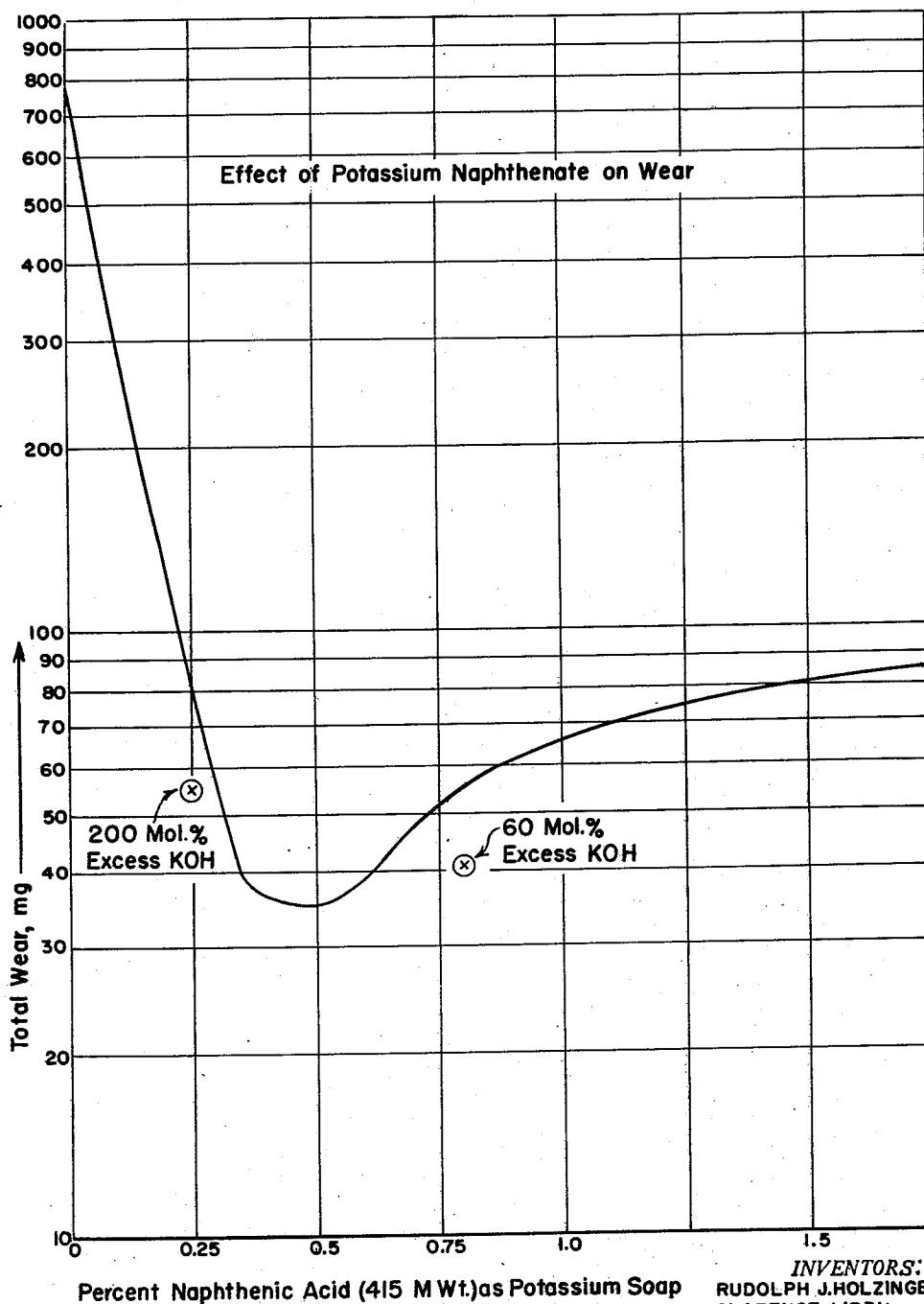


FIG. 6

BY

Charles L. Fuggett
ATTORNEY

1

3,080,322

FIRE-RESISTANT HYDRAULIC FLUIDS

Rudolph J. Holzinger, Haddonfield, Clarence Liddy, Franklinville, and Hans F. Waldmann, Glassboro, N.J., assignors to Socony Mobil Oil Company, Inc., a corporation of New York

Filed June 8, 1961, Ser. No. 115,737

16 Claims. (Cl. 252-75)

This invention relates to an improved composition and method of its preparation and is particularly concerned with improved water-in-oil emulsions useful as fire-resistant hydraulic oils and metalworking oils and their method of preparation. This application is a continuation-in-part application of Serial No. 878,650, filed January 19, 1959.

Hydraulic systems are being employed more and more extensively in industry to operate machinery from remote locations and with comparative ease. Various types of liquids have been employed as the operative fluid in these hydraulic systems; however, for one reason or another, these liquids have been found to lack required properties. Various oils, such as mineral oils, have found much favor in the past; however, many applications of hydraulic systems cannot tolerate leaks with such a pressure transmitting medium since the oil, under high pressure, may then find its way to heat and flame where explosion or combustion occurs. Hydraulic systems are used in metalworking and treating plants and leaks in the system have caused serious accidents in the past.

Water-in-oil emulsions have been tried in the prior art to provide a useful hydraulic oil that had the benefit of low flammability. As long as these emulsions remain unbroken with the water uniformly dispersed throughout the oil in the form of fine particles, the fire resistance remains high. However, adequate stability and anti-wear properties of the emulsion have not been present in prior formulations. The water particles tend to agglomerate in clusters and to settle to the lower part of the reservoir, thereby impairing the fire resistance of the fluid remaining in the upper part. In some cases, an upper layer of clear oil possessing no fire resistance whatsoever will result. In more severe cases, the water may coalesce into larger droplets which eventually will settle out and form a layer of free water on the bottom. In addition to impairment of fire resistance, the latter condition is objectionable in that free water may enter the circulating system and may cause corrosion of lines and working parts and rapid wear of pump parts due to lack of lubrication. It is essential, therefore, that the water particles be dispersed in the oil so that good lubricity is obtained. It is further essential that the water particles be small and uniformly distributed throughout the oil to keep corrosion tendency to a minimum and provide the minimal amount of metal wear. Many prior art emulsions have employed commonly available surface active agents such as esters or partial esters of fatty acids and glycols or polyglycols. Familiar examples are esters of sorbitol and sorbitan sold under the tradenames "Spans" and "Tweens," the latter identifying ethylene oxide derivatives of such esters. However, these agents cannot be employed in alkaline systems since under conditions of high temperature and pressure, the ester linkage is broken and the emulsions become unstable. Consequently, they must be used in neutral or nearly neutral systems. It is well known that in systems containing appreciable amounts of water, it is highly desirable to maintain a distinctly alkaline pH in order to minimize corrosion and corrosive wear.

We have discovered that highly stable and distinctly alkaline emulsions can be prepared by the invention subsequently disclosed.

2

It is an object of this invention to provide an improved water-in-oil emulsion.

A further object of this invention is to provide an improved composition for use as an hydraulic fluid.

5 An additional object of this invention is to provide an improved composition having fire-resisting properties for use as an hydraulic fluid.

10 An additional object of this invention is to provide an improved stable water-in-oil emulsion having fire-resisting properties for use as an hydraulic fluid.

An additional object of this invention is to provide an improved water-in-oil emulsion having anti-wear properties comparable to a mineral oil which is useful as a fire-resistant hydraulic fluid.

15 Another object of this invention is to provide an improved method of preparing water-in-oil emulsions.

These and other important objects will be made apparent in the ensuing detailed discussion of this invention.

20 We have found that a stable, fire-resistant water-in-oil emulsion can be obtained by emulsifying up to 50 percent water with an oil, using a calcium sulfonate as the basic emulsifier and further substantially improved by using selected sodium, potassium, ammonium, lithium, calcium, strontium or barium soaps of naphthenic acids having molecular weights of above about 275 as a stabilizing medium and anti-wear agent.

25 FIGURE 1 shows a plot of percent of oil separation versus potassium naphthenate content and percent of water separation versus naphthenic content after four days storage at 170° F. with 1 percent calcium sulfonate (100% active) as the basic emulsifier.

30 FIGURE 2 shows a plot of percent of oil separation and percent of water separation versus potassium naphthenate content after seven days storage at 170° F. with 1 percent calcium sulfonate (100% active) as the basic emulsifier.

35 FIGURE 3 shows a plot of percent of oil separation and percent of water separation versus potassium naphthenate content after seven days storage at 200° F. with 1 percent calcium sulfonate (100% active) as the basic emulsifier.

40 FIGURE 4 shows a plot of percent of oil separation versus naphthenic acid content and percent of water separation versus naphthenic acid content after seven days storage at 175° F. (total emulsifier content being maintained at 1 percent of total composition).

45 FIGURE 5 shows a plot of percent of oil separation and water separation versus naphthenic acid content of total emulsifier (total emulsifier content being maintained at 1 percent of total composition).

50 The oil used may be any suitable hydrocarbon oil of viscosity range from about 50-400 Saybolt Universal Seconds at 100° F. It has been found, however, that a white oil in that viscosity range provides unusually good results when using the emulsifying and stabilizing agents disclosed hereinafter. This is a completely unexpected result since the rigorous refining required to produce white oils is generally conceded to remove natural inhibitors (see Kalichevsky & Kobe, "Petroleum Refining with Chemicals," Elsevier Publishing Company, 1956), reduce lubricity and greatly interfere with emulsion stability. However, when a white oil is used as the base oil of the emulsion of this invention, improved oxidation resistance and improved emulsion stability are obtained while retaining good lubricity. This can be readily demonstrated by running oxidation tests, such as by A.S.T.M. Standard Method of Test for Oxidation Characteristics of Inhibited Steam-Turbine Oils, A.S.T.M. Designation D-943-54, on the emulsion. The emulsion made using white oil as the base oil shows good oxidation and good emulsion stability. This is clearly a result that could not be predicted from prior knowledge.

The preferred materials for making oil-soluble sulfonates are those obtained by sulfonation of mineral lubricating oil fractions which may be prepared by any of the well known and accepted methods in this art.

The calcium sulfonate used as the basic emulsifier may be present in the blend in the amount of 0.1–5.0 percent by weight of the total blend but preferably about 0.25–2.00 percent by weight can be used to provide entirely satisfactory results. The calcium sulfonate, while primarily an emulsifying agent, supplies a certain amount of anti-corrosive action and anti-wear protection. The calcium sulfonate should have a molecular weight of at least about 900. When the calcium sulfonate has a molecular weight of about 1000 the emulsification is excellent. Particularly useful calcium sulfonates are Calcium Petronate HMW or Basic Calcium Petronate HMW supplied by Sonneborn and Sons, Inc.

It is found that the emulsion will rapidly deteriorate, especially under the influence of heat, when calcium sulfonate is used alone and hence the mixture of calcium sulfonate and oil alone as the oil phase of the hydraulic fluid is for many purposes not satisfactory. However, unusually stable emulsions are found to occur when naphthenic acid soaps of sodium, potassium, ammonium, lithium, calcium, barium or strontium are used as a stabilizing medium. The molecular weight of the naphthenic acid is found to be critical, naphthenic acids of molecular weight less than 275 being found to possess little or no stabilizing action. Particularly useful are naphthenic acids of about 275–1000 molecular weight. Outstanding results are obtained with naphthenic acids identified as Sunaptic Acid "B" and Sunaptic Acid "C" when using sodium, potassium or lithium as the soap forming ingredient. The "B" acid has a molecular weight of 325 whereas the "C" acid has a molecular weight of 415. The "C" acid is somewhat better than the "B" acid, although both provide excellent results. Naphthenic acid identified as Sunaptic Acid "A" having a molecular weight of 295, on the other hand, was found to provide fair but still usable results. This lighter acid reached optimum stability at a lower concentration but this stability was inferior to the stability obtained with the heavier acid and was more critical than that obtained with the heavier acid. A naphthenic acid of molecular weight about 250, designated "D," however, was found to provide little or no benefit regardless of concentration, and regardless of whether the sodium, potassium, ammonium, lithium, calcium, strontium or barium soaps were used. The preferred naphthenic acids are those having molecular weights of about 315–500. The concentration of the stabilizing agent in the finished blend may vary from about 0.1–5.0 percent by weight but preferably should be from about .25–3.0 percent by weight.

In order to insure adequate fire protection, a sufficient amount of water must be properly emulsified into the oil. The water may range from about 10–50 percent of the water-in-oil emulsion; however, a fully acceptable emulsion having excellent fire resisting properties is obtained when the water is about 25–45 percent of the water-in-oil emulsion.

In preparing the emulsions of this invention, it has been found advantageous to form the calcium soap in situ. Thus, a preferred method of preparation calls for dispersing the lime in the water and mixing the dispersion rapidly with the oil containing the calcium sulfonate and naphthenic acid with high speed agitation. Generally, the water phase is added to the oil phase, although in some cases the opposite method may be preferred. The resultant emulsion may be subjected to further mechanical treatment such as passing it through a colloid mill or homogenizer. A suitable method of preparation is as follows: The calcium sulfonate and the naphthenic acid are dissolved in the oil and the mixture is heated to $175 \pm 5^\circ \text{F}$. The water is heated to

$175 \pm 5^\circ \text{F}$. and the lime, after being added to the water, is kept in dispersion by mild agitation. The water phase is then added to the oil phase under vigorous agitation, using a high-speed mixer, followed, if necessary, by further mechanical treatment such as passing the emulsion through a colloid mill or homogenizer. In some cases, it may be desirable to also form the calcium sulfonate in situ. In this case, both the sulfonic acid and the naphthenic acid are dissolved in the oil, with subsequent steps remaining substantially unchanged.

It is desirable and in many cases essential that the amount of lime to be used in preparing these emulsions be sufficient to form the basic soaps of the sulfonic and naphthenic acids and also, if a neutral calcium sulfonate is used to convert the latter to the basic sulfonate. Frequently, it is desirable to employ an amount of lime in excess of the stoichiometric ratio necessary to produce both the basic naphthenate and the basic sulfonate. This excess may, for instance, amount to 50 percent above the stoichiometric ratio and may be as much as 100 percent or more.

Another preferred method of preparing the emulsions of this invention is the following.

This method is particularly preferred when using an alkali of sufficiently high water solubility to form concentrated solutions such as potassium or sodium hydroxide. Two-thirds of the mineral oil and the required amount of naphthenic acid are heated to 150°F . and the required amount of alkali, e.g. potassium hydroxide, in the form of a 50/50 aqueous solution is added with stirring. The temperature is raised to 190°F . and the required amount of calcium sulfonate is added. The temperature of the batch is then raised to $250\text{--}260^\circ \text{F}$. and held for a period of 5–10 minutes. The balance of the mineral oil is added as a quench followed, if desired, by an antioxidant and the batch adjusted to $175\text{ to }185^\circ \text{F}$. The water, separately heated to $175\text{ to }185^\circ \text{F}$., is then added with vigorous agitation and the resultant emulsion processed through a colloid mill or homogenizer to obtain the final, fine particle dispersion.

Rating of the emulsions formed may be done visually either at room temperature or after storage at elevated temperature, e.g., 170°F . A convenient method consists of storing the emulsions in 100 ml. graduated cylinders so that the volume of oil or water separated may be read directly as percent of total volume. Obviously, it is desirable to keep separation of oil and water to a minimum.

In some cases, it is desirable to compare the quality of emulsions without resorting to storage tests. In such cases, a measure of particle size may be had by electrical measurements, e.g., noting the voltage required to obtain current flow between submerged electrodes spaced $\frac{1}{8}$ " apart. In very coarse emulsions of the water-in-oil type, the voltage approaches zero. Where the water is very finely dispersed, the voltage required may exceed 500. Consequently, the higher the voltage reading obtained, the better the emulsion and vice versa.

The following test results demonstrate clearly the magnitude of improvement brought about by the novel emulsifiers. A number of emulsions were prepared using a variable amount of sodium, potassium, ammonium, lithium, calcium, strontium, or barium naphthenate, 1% oil-soluble calcium petroleum sulfonate (1000 M.W.—100% active), 0.5% anti-oxidant, 58.5% 100" U.S.P. White Oil and the balance to 100% water. The emulsions formed were tested for stability at 170°F . and at 200°F . for four days and seven days. The results were graded poor, fair, good and excellent. The standard for excellent required that less than 7% of the oil phase separated after seven days storage at 170°F . or less than 15% of the oil phase separated after seven days storage at 200°F . The standard for excellent further required that no portion of the water phase separated after seven days storage at 170°F .

or less than 2% of the water phase separated after seven days storage at 200° F. The standard for good required that less than 15% of the oil phase separated after seven days storage at 170° F. or less than 30% of the oil phase separated after seven days storage at 200° F. The standard for good further required that less than 2% of the water phase separated after seven days storage at 170° F. or less than 10% of the water phase separated after seven days storage at 200° F. The standard for fair required that less than 35% of the oil phase separated after seven days storage at 170° F. or required more than five days for complete separation at 200° F. The standard for fair also required that less than 50% of the water phase separated after seven days storage at 170° F. The standard for poor required that less than 75% of the oil phase separated after seven days storage at 170° F. or required less than five days for complete separation at 200° F. The standard for poor further required that less than 80% of the water phase separated after seven days storage at 170° F. The standard for bad required that complete separation of the oil and water occur at 170° F. in less than three days or at 200° F. in less than two days. The water-in-oil emulsion using only the basic calcium petroleum sulfonate as emulsifier rated bad. The naphthenates used alone as the emulsifier also rate bad, showing clearly the synergistic action of the sulfonate and selected naphthenate salts. The effect of the molecular weight of the naphthenic acid is clearly shown in Table I as follows:

Table I

	250 M.W. Naphthe- nate	295 M.W. Naphthe- nate	325 M.W. Naphthe- nate	415 M.W. Naphthe- nate
Sodium.....	poor.....	good.....	excellent..	excellent.
Potassium.....	do.....	do.....	do.....	Do.
Lithium.....	do.....	do.....	do.....	Do.
Ammonium.....	do.....	fair.....	fair.....	Do.
Calcium.....	do.....	do.....	do.....	Do.
Strontium.....	do.....	do.....	do.....	Do.
Barium.....	do.....	do.....	do.....	Do.

Some of the data obtained by these tests were plotted on FIGURES 1, 2 and 3 to show the effect of increasing molecular weight of the naphthenic acid, using potassium as the metallic portion of the salt. Four naphthenic acids were selected having molecular weights of 250, 295, 325, and 415. The calcium sulfonate content was maintained constant at 1% and the potassium naphthenate content was varied for each acid. FIGURE 1 shows the water and oil separation of each naphthenate after storage for four days at 170° F. FIGURE 2 shows the water and oil separation after seven days storage at 170° F. FIGURE 3 shows the amount of separation that occurred after seven days storage at 200° F. Obviously, these are exceedingly severe test conditions. The D curve is the 250 molecular weight naphthenic acid; the A curve is the 295 M.W. acid; the B curve is the 325 M.W. acid; and the C curve is the 415 M.W. acid. The curves show that the A, B and C acids provide substantially better stability than the D acid.

Instead of using a constant amount of calcium sulfonate and adding additional amounts of potassium naphthenate, a constant sum of calcium sulfonate and calcium naphthenate was used (1% by weight) and the amount of each soap varied to show the effect of increasing naphthenate concentration. These data were plotted on FIGURE 4, the left half showing separation of oil, the right half showing separation of water. In each half separation without admixture of naphthenic acid to sulfonate is shown on the ordinate at the left, amounting to 30 percent oil and 50 percent water. A broken line is extended from both points across each graph, indicating quality level in the absence of naphthenic acid. In the case of the 295 M.W. acid, increasing amounts effected a slight to moderate improvement in oil and water separation, as shown by the dips in the curves, up to a concentration of about 30 per-

cent. Above this concentration and up to a concentration of about 50 percent—represented by the steep parts of the curves—admixture of naphthenic acid impairs rather than improves emulsion stability. When the acid is used in a concentration above 50 percent and up to a concentration of 100 percent, the emulsions are destroyed completely as indicated by the straight line, horizontal portions of the curves. While the 295 acid is inferior to the higher molecular weight acids, it can be used provided the calcium sulfonate is not reduced below about 1 percent by weight. The 250 M.W. naphthenic acid, on the contrary, gave poor results with respect to emulsion stability regardless of the content of calcium sulfonate used.

Referring again to FIGURE 4, the naphthenic acid of 325 M.W. provides major improvements in oil and water separation; moreover, the concentration of this acid is much less critical, covering an approximate range of from 25 to 85 percent in the case of oil separation, and an approximate range from 20 to 80 percent in the case of water separation. This is indicated by the areas below the broken lines, bounded by the respective curves. This acid is seen to be less sensitive to reduction of calcium sulfonate content.

Naphthenic acid of 415 M.W. effects similar improvements with respect to oil separation, still greater improvements with respect to water separation. Oil separation is reduced from an original level of 30 percent to a level between 10 and 12 percent. Even more important, water separation is reduced from 50 percent to one percent or less. The range of concentration in the latter case is especially broad, covering concentrations from 25 to 95 percent. The largeness of the area below the dotted line, bounded by the curve depicting water separation, is particularly noteworthy.

Having thus established the outstanding utility of naphthenic acid with a molecular weight of 415 in the formulations disclosed hereinbefore, still another series of emulsions were prepared using this acid. In this series, concentration of the naphthenic acid was varied from 0 to 70 percent. Samples of the emulsions thus prepared were stored for two weeks at 140° F., one week at 170° F. and one week at 200° F., and phase separation was noted as before. The results of these tests are depicted in the graph of FIGURE 5. The amount of oil separation is indicated on the curves at the left whereas the amount of water separation is indicated on the curves at the right.

Again, the improvement obtained by using the 415 M.W. naphthenic acid is clear, particularly when used in a concentration from 50 to 70 percent of total emulsifier. For instance, oil separation at 170° F. is reduced from about 60 to about 6 percent. Even more striking, however, is the improvement in storage stability at 200° F. In the absence of the 415 M.W. naphthenic acid, both oil and water separation amounted to 100 percent, the emulsion broke completely, whereas in emulsions containing 60 percent of 415 M.W. naphthenic acid the oil separation was reduced to about 30 percent and the water separation to about 36 percent.

To fully appreciate the magnitude of improvement brought about by this invention, it is necessary to understand the relationship between separation expressed as percent of each phase and expressed as percent of total emulsion volume, as explained below. One hundred ml. of emulsion containing 60 weight percent of oil and 40 weight percent of water contains approximately 66.7 ml. of oil and 33.3 ml. of water. Applying this to the example just quoted, 30 percent oil separation, based on all the oil present, amounts to 30 percent of 66.7 ml. or 20 ml. of separated oil in a 100 ml. emulsion sample. Similarly, 36 percent water separation based on all the water present amounts to 36 percent of 33.3 ml., or 12 ml. of water in a 100 ml. emulsion sample. Therefore, combined separation of oil and water in the emulsion under discussion amounted to 32 ml. in a 100 ml. sample, leaving better than two-thirds of the emulsion intact. It should also be

borne in mind that a storage test conducted for seven days at 200° F. constitutes an unusually severe set of conditions. This is true both from the standpoint of duration and temperature level, which approaches the boiling point of water, one of the main constituents. Consequently, most prior art emulsions break completely when tested in this manner, frequently well before the end of the test period. Consequently, the substantial stability of compositions of this invention taken when subjected to such drastic treatment is surprising and particularly worthy of note. It has been noted hereinbefore that even better results can be obtained by substituting in the naphthenate alkali metals for the alkaline earth metals.

The ratio between calcium sulfonate and the naphthenate may vary from 5/95 to 95/5, depending upon the type and viscosity of the oil and the type and molecular weight of the sulfonate used. The ratios usually employed, however, fall within the range 70/30 to 10/90.

The following Table II gives stability results of a series of emulsions using different metals with 325 M.W. naphthenic acid as the naphthenate stabilizer, the amount being as indicated, and with 1 percent by weight of oil-soluble calcium petroleum sulfonate as the basic emulsifier, about 0.5 percent by weight anti-oxidant, 41.5 percent by weight of water and balance to 100 percent oil. A sample of each emulsion was placed in a tall form 4 oz. oil sample bottle yielding a column height of 130 mm. and subjected to a seven day test at 170° F.

Table II

Run No.	Metal and Amount	Water separated, mm.	Oil separated, mm.
16.....	0.8 K.....	nil.....	7
23.....	0.8 Ba.....	21.....	26
25.....	1.5 Na.....	trace.....	10
26.....	1.5 Li.....	trace.....	8

In the foregoing examples we have shown the effect of soaps derived from selected, high molecular weight naphthenic acids upon the high temperature stability of the water-in-oil emulsions contemplated. Of at least equal importance, however, is an additional discovery we have made, namely, that by judicious selection of molecular weight of acid, type of alkali and concentration of soap, pump wear can be controlled. This can be demonstrated as follows.

Various amounts of potassium soap prepared from naphthenic acid of molecular weight 415 and stoichiometric equivalents of potassium hydroxide were added to a "base formula" consisting of the following ingredients:

	Percent by weight
Water	40.0.
Mixture of octylated and styrenated diphenylamines (Agerite Stalite)	0.5.
Basic calcium petroleum sulfonate (M. Wt. 1000—40 percent active)	2.5.
Potassium naphthenate	Varying amounts.
100 SUS paraffin oil	To make 100.0

The resultant compositions were then evaluated as to their wear characteristics.

A recognized test for lubricating capabilities, the so-called Vickers Pump Test, may be achieved by circulating the fluid in a Vickers pump, such as Vickers Vane Type Pump, Model V-111-E10 (rated at 2 gal. per. min.), manufactured by Vickers Incorporated, of Detroit, Michigan. This is a positive displacement, vane-type hydraulic pump. The rotor with twelve steel vanes in contact with a steel ring, turns at 1200 r.p.m. The twelve vanes and the ring are weighed before and after the test, and the weight of metal worn off during the test is determined by

difference. The pump test stand has a five gallon fluid reservoir and up to 2.5 gallons of fluid per minute are circulated at 1000 p.s.i. pressure. A convenient duration of test is 100 hours, preferably run at a temperature of 175° F. to simulate the severe operating conditions which hydraulic oils very frequently encounter in service. Wear in the Vickers pump occurs both on the vanes and on the ring. Vane wear is highly important and critical in the operation of the pump. Ring wear, although less important, still is of significance. Since pumps of this general type are widely used in hydraulic systems, capability of a hydraulic fluid, as a lubricant, to minimize such wear, is a necessity.

The results obtained with respect to wear are shown in FIGURE 6, plotted against naphthenic acid concentration present in the form of potassium naphthenate.

It will be noted that calcium petroleum sulfonate, when used alone (0% soap concentration), produces very high wear. It will also be noted that the use of as little as 0.25% potassium naphthenate produces a drastic decrease in wear. This effect is enhanced or essentially maintained when naphthenic acid concentration is raised up to about 0.5%. Above this level, further increases in naphthenate content cause only a very gradual increase in wear, indicating soap concentration to be relatively non-critical. It is also noteworthy that even at the highest naphthenate concentration, i.e., 1.5% wear is still well below the value for the composition containing the sulfonate only, with a wear of 81 mg. as compared to 759 mg.

In addition to examples using stoichiometric amounts of potassium hydroxide, we have also prepared two compositions using an excess of this alkali. These examples and their effect on wear are likewise shown in FIGURE 6. For instance, the use of 200 mol percent excess with a soap prepared from the same acid and used in a concentration of 0.25% resulted in a further reduction of wear, i.e., from a value of 80 mg. to a value of 55 mg. A similar wear reduction can be seen from the use of excess alkali with a naphthenic acid concentration of 0.8% as the soap. It is evident, therefrom, that an excess of alkali over the stoichiometric amount tends to be beneficial and renders concentration of soap employed even less critical.

The use of ammonia to prepare ammonium naphthenate soaps may lead to compositions which tend to lose alkali by volatilization, especially under high temperature conditions. Such a loss can be counteracted by the use of alkali in excess over the stoichiometric equivalent as described above. Moreover, volatilization may provide additional benefits such as corrosion inhibition in the vapor phase.

Thus, we have shown that over a fairly wide range of soap concentration, optimum performance of the fluid can be attained. We have shown in FIGURES 1, 2 and 3 that this concentration range also produces very substantial benefits as to stability. Thus, we are enabled to combine in the same composition optimum performance in the most important aspects of an emulsion hydraulic fluid, namely, colloidal stability and wear.

The detailed description of the invention given hereinabove and the examples supplied are not intended to limit the scope of the invention. The only limitations intended are those found in the claims attached hereto.

We claim:

1. A composition for use as hydraulic fluid consisting essentially of a water-in-oil emulsion containing 0.1–5.0 percent by weight of oil-soluble calcium petroleum sulfonate and 0.1–5.0 percent by weight of a soap of naphthenic acids having a molecular weight greater than 275, the cation of the soap being selected from the group consisting of sodium, potassium, ammonium, lithium, calcium, strontium, and barium, the oil portion of said emulsion being a hydrocarbon oil of from about 50–400 S.U.S. viscosity at 100° F., the water content of said emulsion being about 10–50 percent by weight, and the ratio be-

tween the oil-soluble calcium petroleum sulfonate and the metal naphthenate being from about 5/95 to 95/5 by weight.

2. A composition for use as hydraulic fluid consisting essentially of a water-in-oil emulsion containing about 0.1–5.0 percent by weight of oil-soluble calcium petroleum sulfonate and about 0.1–5.0 percent by weight of soaps of naphthenic acids having molecular weights of about 275–1000, the cation of the soap being selected from the group consisting of sodium, potassium, ammonium, lithium, calcium and barium, the oil portion of said emulsion being a hydrocarbon oil of from about 50–400 S.U.S. viscosity at 100° F., the water content of said emulsion being about 10–50 percent by weight and the ratio between the oil-soluble calcium petroleum sulfonate and the metal naphthenate being from about 5/95 to 95/5 by weight.

3. A composition for use as hydraulic fluid consisting essentially of a water-in-oil emulsion in which about 10–50 percent by weight of the mixture is water uniformly distributed in fine-particle form and containing about 0.1–5.0 percent by weight of oil-soluble calcium petroleum sulfonate as an emulsifying agent and about 0.1–5.0 percent by weight of soaps of naphthenic acids having molecular weights of about 315–500 as a stabilizing medium whereby the emulsion is retained with the water particles in fine-particle form and uniformly distributed throughout the mixture, the cation of the soap being selected from the group consisting of sodium, potassium, ammonium, lithium, calcium, strontium and barium, the oil portion of said emulsion being a hydrocarbon oil of from about 50–400 S.U.S. viscosity at 100° F. and the ratio between the oil-soluble calcium petroleum sulfonate and the metal naphthenate being from about 5/95 to 95/5 by weight.

4. A composition for use as hydraulic fluid consisting essentially of a water-in-oil emulsion in which about 25–45 percent by weight of the mixture is water uniformly distributed in fine-particle form and containing about 0.25–2.00 percent by weight of oil-soluble calcium petroleum sulfonate as an emulsifying agent and about 0.25–3.0 percent by weight of soaps of naphthenic acids having molecular weights of about 315–500 as a stabilizing medium, the cation of the soap being selected from the group consisting of sodium, potassium, ammonium, lithium, calcium, strontium and barium, whereby the emulsion is retained with the water particles in fine dispersion in the oil, the oil portion of said emulsion being a hydrocarbon oil of from about 50–400 S.U.S. viscosity at 100° F., and the ratio between the oil-soluble calcium petroleum sulfonate and the metal naphthenate being from about 5/95 to 95/5 by weight.

5. A composition for use as hydraulic fluid consisting essentially of a water-in-oil emulsion in which 25–45 percent by weight of the mixture is water uniformly distributed in fine-particle form, the oil is a white oil of about 50–400 S.U.S. viscosity at 100° F. and the mixture contains about 0.25–2.00 percent by weight of oil-soluble calcium petroleum sulfonate as an emulsifying agent and about 0.25–3.00 percent by weight of soaps of naphthenic acids having molecular weights of about 315–500 as a stabilizing medium, the cation of the soap being selected from the group consisting of sodium, lithium, potassium, ammonium, calcium, strontium and barium, whereby the emulsion is retained with the water particles in fine dispersion in the oil, the ratio between the oil-soluble calcium petroleum sulfonate and the metal naphthenate being from about 5/95 to 95/5 by weight.

6. A composition for use as hydraulic fluid consisting essentially of a water-in-oil emulsion in which about 25–45 percent by weight of the mixture is water uniformly distributed in fine-particle form, the oil is a white oil of about 50–400 S.U.S. viscosity at 100° F. and the mixture contains about 0.25–2.00 percent by weight of oil-soluble calcium petroleum sulfonate as an emulsifying agent and

about 0.25–3.00 percent by weight of soaps of a naphthenic acid having a molecular weight of 325 as a stabilizing medium, the cation of the soap being selected from the group consisting of sodium, potassium, lithium, ammonium, calcium, strontium and barium, whereby the emulsion is retained with the water particles in fine dispersion in the oil, the ratio between the oil-soluble calcium petroleum sulfonate and the metal naphthenate being from about 5/95 to 95/5 by weight.

7. A composition for use as hydraulic fluid consisting essentially of a water-in-oil emulsion in which about 25–45 percent by weight of the mixture is water uniformly distributed in fine-particle form, the oil is a white oil of about 50–400 S.U.S. viscosity at 100° F. and the mixture contains about 0.25–2.00 percent by weight of oil-soluble calcium petroleum sulfonate as an emulsifying agent and about 0.25–3.00 percent by weight of soaps of naphthenic acid having a molecular weight of 415 as a stabilizing medium, the cation of the soap being selected from the group consisting of sodium, potassium, ammonium, lithium, calcium, strontium and barium, whereby the emulsion is retained with the water particles in fine dispersion in the oil, the ratio between the oil-soluble calcium petroleum sulfonate and the calcium naphthenate being from about 5/95 to 95/5 by weight.

8. A composition for use as hydraulic fluid consisting essentially of a water-in-oil emulsion containing about 0.25–2.00 percent by weight of oil-soluble calcium petroleum sulfonate, about 0.25–3.00 percent by weight of naphthenic acids having a molecular weight of 315–500, an amount of calcium hydroxide substantially in excess of that required to produce the basic calcium sulfonate, an amount of an hydroxide substantially in excess of that required to produce the basic soaps of the naphthenic acids, the cation of the soap of said hydroxide being selected from the group consisting of sodium, potassium, ammonium, lithium, calcium, strontium and barium, the oil portion of said emulsion being a hydrocarbon oil of from about 50–400 S.U.S. viscosity at 100° F., the water content of said emulsion being about 10–50 percent by weight, and the ratio between the oil-soluble calcium petroleum sulfonate and the metal naphthenate being from about 5/95 to 95/5 by weight.

9. The composition of claim 8 further characterized in that the excess of calcium hydroxide is limited to about 100 percent greater than that required to produce basic calcium sulfonate and the excess of metal hydroxide is limited to about 100 percent greater than that required to produce basic metal naphthenate.

10. The composition of claim 8 further characterized in that the excess of calcium hydroxide is limited to about 50 percent greater than that required to produce basic calcium sulfonate and the excess of metal hydroxide is limited to about 50 percent greater than that required to produce basic metal naphthenate.

11. The method of preparation of a water-in-oil emulsion which comprises the steps: dissolving naphthenic acids and oil-soluble calcium petroleum sulfonate in the base oil, the oil being a hydrocarbon oil of from about 50–400 S.U.S. viscosity at 100° F., dispersing lime in the water, combining the oil phase with the aqueous phase in such a manner as to simultaneously effect both formation of basic calcium salts and emulsification, the amount of oil-soluble petroleum sulfonate being 0.1–5.0 percent by weight of the total blend, the amount of calcium naphthenate being 0.1–5.0 percent by weight of the total blend, the ratio between the oil-soluble calcium petroleum sulfonate and the calcium naphthenate being from about 5/95 to 95/5 by weight and the molecular weight of the naphthenic acid used to form the calcium naphthenate having a molecular weight greater than 315.

12. A composition for use as hydraulic fluid consisting essentially of a water-in-oil emulsion containing about 0.1–5.0 percent by weight of oil-soluble calcium petro-

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leum sulfonate and about 0.1–5.0 percent by weight of the potassium soap of naphthenic acids having molecular weights of about 275–1000, the oil portion of said emulsion being a hydrocarbon oil of from about 50–400 S.U.S. viscosity at 100° F., the water content of said emulsion being about 10–50 percent by weight and the ratio between the oil-soluble calcium petroleum sulfonate and the potassium naphthenate being from about 5/95 to 95/5 by weight.

13. A composition for use as hydraulic fluid consisting essentially of a water-in-oil emulsion in which about 10–50 percent by weight of the mixture is water uniformly distributed in fine-particle form and containing about 0.1–5.0 percent by weight of oil-soluble calcium petroleum sulfonate as an emulsifying agent and about 0.1–5.0 percent by weight of the potassium soap of naphthenic acids having molecular weights of about 315–500 as a stabilizing medium whereby the emulsion is retained with the water particles in fine-particle form and uniformly distributed throughout the mixture, the oil portion of said emulsion being a hydrocarbon oil of from about 50–400 S.U.S. viscosity at 100° F. and the ratio between the oil-soluble calcium petroleum sulfonate and the potassium naphthenate being from about 5/95 to 95/5 by weight.

14. The composition of claim 13 further characterized in that the molecular weight of the naphthenic acid is 325.

15. The composition of claim 13 further characterized in that the molecular weight of the naphthenic acid is 415.

16. The method of preparation of a water-in-oil emulsion which comprises the steps: mixing a portion of the base oil with naphthenic acid, heating the mixture to

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about 150° F., adding with stirring a dilute solution of an alkali selected from the group consisting of sodium hydroxide, lithium hydroxide, potassium hydroxide, ammonium hydroxide, calcium hydroxide, strontium hydroxide and barium hydroxide, raising the temperature of the mixture to about 190° F., adding with stirring oil-soluble calcium petroleum sulfonate, raising the temperature of the mixture to about 250° F. and holding the mixture at that temperature for a period of about 5–10 minutes, adding with stirring the remainder of the base mineral oil, separately heating the balance of the water to about 175–185° F., and adding the heated water to the mixture with vigorous agitation to form the finished water-in-oil stable emulsion, the amount of oil-soluble calcium petroleum sulfonate being 0.1–5.0% by weight of the total blend, the amount of naphthenic acid salt formed by the mixture being 0.1–5.0% by weight of the total blend, the ratio between the oil-soluble calcium petroleum sulfonate and the naphthenic acid salt being from about 5/95 to 95/5 by weight of the molecular weight of the naphthenic acid used to form the naphthenic acid salt having a molecular weight of about 275/1000.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,080,322

March 5, 1963

Rudolph J. Holzinger et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 15, for "Serial No. 878,650" read --
Serial No. 787,650 --; column 7, line 9, strike out "taken".

Signed and sealed this 17th day of December 1963.

SEAL)
test:

NEST W. SWIDER

testing Officer

EDWIN L. REYNOLDS

Acting Commissioner of Patents

