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(54) **Method for controlling the quality of an emulsion.**

(57) The rate at which an emulsion of a viscous oil in water emulsion may deteriorate in storage is reduced by adding to the emulsion an aqueous solution of a surfactant and allowing the emulsion and added aqueous surfactant to remain in contact with each other. The surfactant is preferably mixed with the emulsion by gentle stirring. The emulsions are preferably combustible fuel emulsions and the oil may be a heavy crude oil or a residue from a petroleum refining process. The surfactant is preferably a non-ionic surfactant, most preferably an alkyl phenol ethoxylate.

This invention relates to a method for controlling the quality of an emulsion of a viscous oil in water, particularly an emulsion intended for combustion as a fuel, by arresting or reducing the rate at which the emulsion may deteriorate when subjected to prolonged standing, for example in storage tanks.

Emulsion fuels prepared from viscous oils have been previously described in the patent literature and elsewhere. For example, GB 974042 discloses a fuel composition comprising an oil-in-water emulsion of a petroleum oil having a viscosity above 40 SSF at 122°F, the amount of water in said emulsion being such that said emulsion has a viscosity of less than 150 SSF at 77°F and the said oil comprising at least 60 volume per cent of the emulsion.

The oils which are emulsified are generally viscous oils which in their non-emulsified state are too viscous to be pumped and require high preheat temperatures to be atomised successfully in combustion equipment.

Large deposits of viscous oils occur in several parts of the world, eg in Canada, USA, USSR and Venezuela. It is likely that emulsified fuels will become more commercially important in the future as the need to exploit the aforementioned deposits increases.

Such emulsified fuels are generally stable, some more so than others, depending on the method of production.

However, on prolonged storage, eg over a period of months or years, there may be a tendency for some emulsions to deteriorate somewhat, eg for the mean particle size of the droplets to increase, for the particle size distribution to widen and for the emulsions to become more susceptible to shear degradation, for example, in pumps, valves or at burner tips. This can give rise to problems in handling and combusting the emulsions.

GB 2220673-A discusses the problems of deteriorated, ultraheavy emulsion fuels and proposes methods for the regeneration of such deteriorated emulsions. If the deterioration is slight, a non-ionic surfactant is added to the deteriorated emulsion and the resulting mixture is subjected to high shear agitation. If the deterioration is more severe, an anionic surfactant is added, the mixture is sheared and a non-ionic surfactant is added. Alternatively, an anionic surfactant and a non-ionic surfactant are both added and the mixture is then sheared.

GB 2220673-A is concerned with a remedial treatment to restore the quality of an emulsion after significant deterioration has occurred.

We have now devised a preventative method for maintaining the quality of an emulsion of a viscous oil in water, which may have a tendency to deteriorate in storage, by reducing the rate at which it may deteriorate.

Thus according to the present invention there is provided a method for reducing the rate at which an emulsion of a viscous oil in water may deteriorate in storage by adding to the emulsion an aqueous solution of a surfactant and allowing the emulsion and added aqueous surfactant to remain in contact with each other.

In order to avoid the unnecessary use of surfactant, since the emulsion may be used before it has deteriorated or deteriorated to any significant extent, it may be advisable not to add the surfactant until signs of deterioration are noted.

Thus according to a further feature of the invention there is provided a method for reducing the rate at which an emulsion of a viscous oil in water may deteriorate in storage by monitoring the emulsion and, if signs of deterioration are noted, by adding to the emulsion an aqueous solution of a surfactant and allowing the emulsion and added aqueous surfactant to remain in contact with each other for the remainder of the period of storage.

The surfactant solution may simply be added to the emulsion but preferably, if facilities permit, it is mixed with the emulsion by low shear rate mixing, for example at a shear rate below 100 reciprocal seconds. Paddle mixers, which are sometimes present in storage tanks, are suitable for this purpose.

It has been found that simply adding the surfactant to a deteriorating emulsion, or one with the potential for deterioration, reduces the rate of deterioration but phase separation may occur. When the surfactant is mixed in, phase separation does not occur and the reduction effect is enhanced.

The emulsions may be monitored by carrying out regular determinations of oil droplet size.

Emulsion droplet size distribution data may be obtained by using a Coulter Counter, a Malvern Multisizer, a Galai CIS or other suitable instrument.

The method is particularly suitable for treating combustible emulsions intended for use as fuels derived from combustible oils, such as naturally occurring heavy crude oils. Such crude oils will generally have API gravities in the range 5° to 20° and include Wolf Lake and Lake Marguerite crude oil from Alberta, bitumen from the Canadian tar sands, Hewitt crude oil from Oklahoma and heavy oils from the Orinoco oil belt in Venezuela.

Combustible emulsions prepared from viscous products, by-products and waste products of the petroleum, petrochemical and chemical industries are also very suitable. Such materials include atmospheric and vacuum residues from the distillation of lighter crude oils and visbreaker residues.

Emulsions not intended for combustion which may be treated include paint emulsions, agrochemical emulsions, etc.

Suitable surfactants may be non-ionic, anionic or cationic, but are preferably non-ionic. Clearly they must be compatible with the surfactant originally used in preparing the emulsion. This is best achieved by using a

member of the same family, if not the same surfactant.

Preferred non-ionic surfactants are ethoxylated alkyl phenols, but ethoxylated secondary alcohols, ethoxylated amines and ethoxylated sorbitan esters are also suitable.

5 The most preferred ethoxylated alkyl phenols are nonyl phenols containing 15 to 30 ethylene oxide units per molecule.

An ethoxylated nonyl phenol containing about 20 ethylene oxide units is very suitable.

Suitable anionic surfactants include alkyl, aryl and alkaryl sulphates, sulphonates and phosphates.

Suitable cationic surfactants include quaternary ammonium compounds and n-alkyl diamines and triamines in acidic form.

10 The surfactant is suitably added in the form of a fluid aqueous solution containing 10 - 30% by weight or 80 - 90% by weight surfactant, preferably about 25% by weight. Between 30% and 80% by weight surfactant, the solution is more viscous.

The quantity of surfactant added is suitably in amount 0.005 to 1%, preferably 0.1 to 0.7 %, by weight of the weight of the original emulsion.

15 The invention is illustrated with reference to the following Example.

Example

20 An emulsion fuel containing approximately 30% by volume water and 70% by volume of a viscous crude oil from the Orinoco oil belt was kept in a storage tank over a period of several months.

After about six months it became apparent from droplet size analysis that the quality of the emulsion in the tank was deteriorating.

Experiments were carried out to investigate the effect of surfactant addition to samples of the emulsion.

The mean droplet size of the oil in the emulsion was 24.6µm at the beginning of the experiments.

25 The surfactant chosen was a nonylphenol ethoxylate containing 20 ethylene oxide groups per molecule (NP20). It was used in the form of a 25% by weight solution in de-ionised water.

Three surfactant concentrations were investigated:

6.25 x 10⁻³ % w/w NP20/Emulsion

6.25 x 10⁻² % w/w NP20/Emulsion

30 6.25 x 10⁻¹ % w/w NP20/Emulsion

The surfactant solution was added to the emulsion in the first instance with no stirring and in the second instance with gentle manual stirring, at a shear rate below 100 reciprocal seconds, thus simulating large tank mixers or recirculation systems.

200g samples of each of these blends were stored in an oven at 30°C to simulate tank storage conditions. 35 Control samples, containing no additional surfactant, were also placed in the oven.

Emulsion quality was monitored by measuring the mean droplet size at weekly intervals for five weeks and after nine weeks, and by measuring the results of shearing the samples at 20°C and 70°C after nine weeks using a Citenco mixer, operating under medium shear conditions of 5,500 rpm. The 200g samples were subdivided in order to perform the tests at the two temperatures.

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Addition of Surfactant without Mixing

The surfactant solution diffused downwardly through the samples which separated into a surfactant phase and an emulsion phase by the end of week one, the quantity of surfactant separated being similar to that added 45 initially. The experiment was continued, however, to assess if the added surfactant still had any effect.

Table 1 shows the trends in mean droplet sizes throughout the test period. The control sample showed a steady increase in droplet size from 24.5µm initially, to 36.1µm at the end of week 9. Adding surfactant to the emulsion, with no mixing, slows the increase in droplet size, but does not arrest it completely. Some dependence on surfactant concentration was observed.

50 Results from the shearing tests are given in Table 2 for the three surfactant concentrations. It should be noted that the phase-separated surfactant was mixed into the emulsion before commencing the shearing test. The results obtained at 20°C show increases in droplet size over the test period for the two lowest surfactant concentrations. At the highest surfactant concentration, the emulsion droplet size remained either the same or decreased slightly. The droplet size for the control sample (containing no additional surfactant) increased from 55 31.3 to 47.8 µm during testing.

Shearing results obtained at 70°C show that the emulsions containing the two lowest concentrations of additional surfactant broke after mixing for 150 seconds. The sample containing 0.6% additional surfactant showed a decrease in droplet size (32.6 to 10.4µm) over the test period. The control sample broke after 20 sec

mixing at 70°C.

Addition of Surfactant with Mixing

Results are given in Table 3. Whilst it is evident from these results that mixing the surfactant into the emulsion is better than no mixing, there is still a gradual increase in droplet size over the test period. The highest surfactant addition again had the most positive effect.

Shearing results are summarised in Table 4. At 20°C, mean droplet size was not significantly affected at any of the surfactant concentrations investigated. At 70°C, the sample containing 0.006 % added surfactant showed a slight decrease in mean droplet size (30.5 to 25.2µm) over the test period.

The results lead to the following conclusions:

Addition of surfactant to an emulsion in the presence or absence of gentle mixing reduces the rate of emulsion deterioration.

Addition of surfactant to an emulsion with no mixing, results in sample phase separation into an emulsion and a surfactant layer within one week.

When the surfactant was gently mixed into the emulsion no phase separation occurred and the rate was reduced still further.

The results of shearing at both 20 and 70°C is improved by the addition of more surfactant whether or not the surfactant is mixed in.

TABLE 1: TRENDS IN MEAN DROPLET SIZE (µm), WEEKS 1 - 9
ADDITIONAL SURFACTANT NOT MIXED IN

Surfactant Concentration, % wt	Mean Droplet Size			
	0.006	0.06	0.6	Control
Week: 1	26.7	25.0	23.7	25.8
2	28.4	27.1	25.6	27.8
3	29.2	27.7	29.2	31.5
4	27.7	28.0	27.4	32.6
5	28.2	28.2	27.7	33.2
9	33.9	32.4	32.3	36.1

Note: Emulsion Initial mean droplet size = 24.6µm

TABLE 2: SHEARING RESULTS (μm)
 ADDITIONAL SURFACTANT NOT MIXED IN

Surfactant Conc.	Mean Droplet Size							
	0.006%		0.06%		0.6%		Control	
	20 C	70 C	20 C	70 C	20 C	70 C	20 C	70 C
0	35.0	30.0	24.6	29.4	32.8	32.6	31.3	33.5
10	32.3	48.6	31.0	44.1	33.8	24.3	36.8	73.9
20	36.7	54.2	23.0	56.6	32.1	20.2	37.5	103.1
30	36.2	72.3	33.0	55.5	33.8	19.3	36.2	-----
60	37.1	84.3	34.7	58.8	31.3	13.8	36.9	
90	37.1	93.9	36.7	67.8	29.9	11.5	35.8	
120	41.2	104.7	33.1	69.6	27.8	12.0	42.0	
150	43.4	-----	37.6	-----	32.1	10.5	38.0	
180	41.4		40.7		27.3	10.4	47.8	

Note: Partitioned surfactant mixed into emulsion layer before
 commencing dynamic stability test.

("-----" - sample inverted at this point.

TABLE 3: TRENDS IN MEAN DROPLET SIZE (μm) WEEKS 1-9
ADDITIONAL SURFACTANT MIXED IN

Surfactant Concentration, %wt	Mean Droplet Size			
	0.006	0.06	0.6	Control
Week: 1	23.9	20.1	20.2	25.8
2	28.4	27.1	25.6	27.8
3	30.5	24.3	24.2	31.5
4	31.3	27.1	25.2	32.6
5	30.0	28.1	27.9	33.2
9	34.5	30.1	28.0	36.1

Note: Emulsion Initial mean droplet size = $24.6\mu\text{m}$

TABLE 4: SHEARING RESULTS (μm)

ADDITIONAL SURFACTANT MIXED IN

Surfactant Conc.	Mean Droplet Size							
	0.006%		0.06%		0.6%		Control	
Mixing time Seconds	20 C	70 C	20 C	70 C	20 C	70 C	20 C	70 C
0	33.0	36.5	33.0	31.2	28.6	30.5	31.3	33.5
10	32.8	65.5	32.1	42.3	29.5	31.8	36.8	73.9
20	34.3	74.2	33.4	51.5	32.3	27.4	37.5	103.1
30	31.4	81.9	31.1	61.9	31.3	26.2	36.2	-----
60	36.8	-----	35.5	62.9	30.9	24.5	36.9	
90	43.6		33.9	62.7	32.8	23.8	35.8	
120	29.3		34.8	61.5	28.9	21.7	42.0	
150	26.5		31.2	65.8	31.1	26.0	38.0	
180	33.7		36.3	72.8	32.4	25.2	47.8	

("-----" - sample inverted at this point.

Claims

1. A method for reducing the rate at which an emulsion of a viscous oil in water may deteriorate in storage characterised by the fact that an aqueous solution of a surfactant is added to the emulsion and the emulsion and the added aqueous surfactant are allowed to remain in contact with each other.
2. A method according to claim 1 for reducing the rate at which an emulsion of a viscous oil in water may deteriorate in storage characterised by the fact that the emulsion is monitored and, if signs of deterioration are noted, an aqueous solution of a surfactant is added to the emulsion and the emulsion and added surfactant are allowed to remain in contact with each other for the remainder of the period of storage.
3. A method according to either of the preceding claims characterised by the fact that the surfactant solution is simply added to the emulsion.
4. A method according to either of claims 1 or 2 characterised by the fact that the surfactant is mixed with the emulsion by low shear rate mixing.

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5. A method according to claim 4 wherein the shear rate of mixing is below 100 reciprocal seconds.
 6. A method according to any of claims 2 to 5 wherein the emulsion is monitored by carrying out regular determinations of the oil droplet size.
 7. A method according to any of the previous claims wherein the emulsion is a combustible emulsion derived from a combustible oil.
 8. A method according to claim 7 wherein the oil is a heavy crude oil having an API gravity in the range 5° to 20°.
 9. A method according to claim 7 wherein the oil is an atmospheric residue, a vacuum residue or a visbreaker residue.
 10. A method according to any of the preceding claims wherein the surfactant is a non-ionic surfactant.
 11. A method according to claim 10 wherein the non-ionic surfactant is an ethoxylated alkyl phenol.
 12. A method according to claim 11 wherein the ethoxylated alkyl phenol is an ethoxylated nonyl phenol containing 15-30 ethylene oxide units per molecule.