

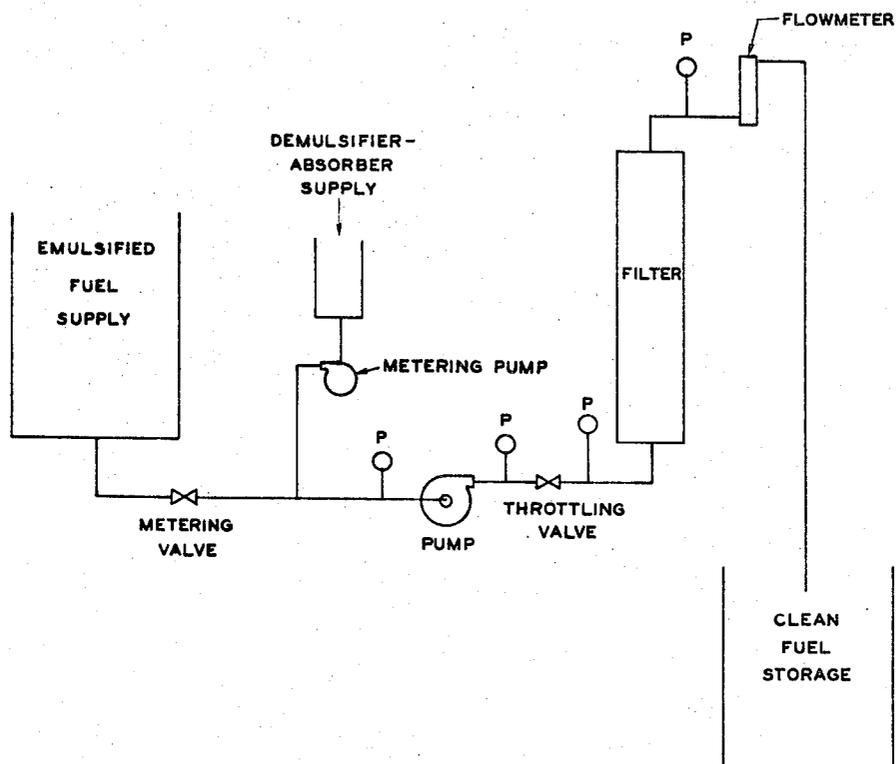
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METHOD OF RESOLVING THIXOTROPIC JET AND ROCKET FUEL EMULSIONS

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3,378,418  
**METHOD OF RESOLVING THIXOTROPIC JET  
AND ROCKET FUEL EMULSIONS**  
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**ABSTRACT OF THE DISCLOSURE**

A process of resolving jet and rocket thixotropic hydrocarbon-in-water emulsions comprising water, an emulsifiable hydrocarbon and an emulsifying agent, said hydrocarbon being present in said emulsion fuel in an amount of at least 80% hydrocarbon by volume of the emulsion, which process is characterized by contacting said emulsion with a substantially insoluble breaker-absorber such as argillaceous earth or clayey materials, thereby breaking the emulsion and also removing the water-type external phase.

This invention in general relates to certain thixotropic emulsions.

In the following copending patent applications: S.N. 286,877 filed May 20, 1963 (relating to certain unique thixotropic emulsions), now abandoned; S.N. 302,001, filed Aug. 14, 1963 (relating in general to certain unique thixotropic hydrazine emulsions); S.N. 302,177, filed Aug. 14, 1963, (relating to certain unique thixotropic jet and rocket fuel emulsions), now abandoned; and S.N. 411,103, filed Nov. 13, 1964, (relating to process of continually preparing these unique emulsions); there are disclosed certain thixotropic emulsions and systems relating thereto. These patent applications are, by reference, incorporated into the present application as if part hereof.

The advantages of the emulsified fuels described in the above patent applications have been demonstrated. Among other things, it has been found that when liquid fuels are subjected to crashes or military action and exposed to firearms or other means of ignition under fire power, serious fires and explosions often result. However, when emulsified fuels are subjected to crashes or to firearms or other fire power, the danger from serious fires and explosions is substantially reduced or eliminated.

In using fuels in conventional systems such as jet engines which have not been adopted to employ emulsified fuels, it is necessary to revert the emulsified fuel to the liquid fuel itself. When reversion is effected, the external phase becomes suspended in the fuel. This requires lengthy and difficult separations before a fuel will meet original specification so it can be employed as a fuel in conventional engines, such as in jet engines.

Although emulsions of these types can be resolved by subjecting them to shear and/or demulsifiers, the emulsions often invert under such treatment thus resulting in a dispersion of the original minor external phase in the major internal phase. This poses certain problems. For example, when the thixotropic emulsified fuel is inverted, it is necessary to remove the original external phase before it can be used in certain fuel systems because demulsification often produces a course dispersion of water in the fuel—thus making it unacceptable for military applications.

In certain instances, separation of these particles can

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be effected by allowing the dispersion to stand undisturbed for a sufficient length of time so that the suspended water particles can settle out. However, as a practical matter, the time required for settling and the size of the equipment required to achieve this is too impractical for military field use.

I have now discovered that emulsified fuels can be readily resolved to yield a satisfactory fuel by contacting the emulsion with a material capable of breaking the emulsion, which material is also immiscible in either phase. For example, the emulsion can be broken and the external phase removed by employing a solid breaker-absorber capable of both breaking the emulsion and absorbing the external phase so that the internal phase is recovered without contamination. Thus, when a hydrophilic insoluble solid such as clay is contacted with the emulsion, the emulsion is not only broken but the external phase is absorbed on the clay which is removed by any suitable means such as settling, centrifugation, filtration, electrostatic precipitation and the like. For ease of operation a small filtration unit is preferred.

In summary, the breaker-absorber not only breaks the emulsion but also removes the water-type external phase.

The unique thixotropic emulsions described herein have been amply described in the above patent applications. It should be noted that these emulsions can be prepared by any suitable emulsifying agent. Although oxyalkylates are preferred, other types of suitable emulsifiers can be employed.

By using the means of selecting suitable emulsifiers described in the above applications, one can select and employ emulsifiers, for example, of the following types:

I. Anionic

- (A) Carboxylic acids:
  - (1) Carboxyl joined directly to the hydrophobic group (subclassification on basis of the hydrophobic group), e.g. fatty acids, soaps, rosin soaps, etc.
  - (2) Carboxyl joined through an intermediate linkage.
    - (a) Amide group as intermediate link.
    - (b) Ester group as intermediate link.
    - (c) Sulfoamide group as intermediate link.
    - (d) Miscellaneous intermediate links, ether, —SO<sub>2</sub>—, —S—, etc.
- (B) Sulfuric esters (sulfates):
  - (1) Sulfate joined directly to hydrophobic group.
    - (a) Hydrophobic group contains no other polar structures (sulfated alcohol and sulfated olefin type).
    - (b) Sulfuric esters with hydrophobic groups containing other polar structures (sulfated oil type).
  - (2) Sulfate group joined through intermediate linkage.
    - (a) Ester linkage (Artic Syntex M. type).
    - (b) Amide linkage (Xynomine type).
    - (c) Ether linkage (Triton 770 type).
    - (d) Miscellaneous linkages (e.g., oxyalkylimidazole sulfates).
- (C) Alkane sulfonic acids:
  - (1) Sulfonic group directly linked
    - (a) Hydrophobic group bears other polar substituents ("highly sulfated oil" type). Chloro, hydroxy, acetoxy, and olefin sulfonic acids (Nytron type).

- (b) Unsubstituted alkane sulfonic acids (MP 189 type; also cetane sulfo acid type).
- (c) Miscellaneous sulfonic acids of uncertain structure, e.g., oxidation products of sulfurized olefins, sulfonated rosin, etc.
- (2) Sulfonic groups joined through intermediate linkage.
- (a) Ester linkage.
- (1)  $\text{RCOO}-\text{X}-\text{SO}_3\text{H}$  (Igepon AP type).
- (2)  $\text{ROOC}-\text{X}-\text{SO}_3\text{H}$  (Aerosol and sulfacetate type).
- (b) Amide linkage.
- (1)  $\text{RCONH}-\text{X}-\text{SO}_3\text{H}$  (Igepon T type).
- (2)  $\text{RNHOC}-\text{X}-\text{SO}_3\text{H}$  (sulfosuccinamide type).
- (c) Ether linkage (Triton 720 type).
- (d) Miscellaneous linkages and two or more linkages.
- (D) Alkyl aromatic sulfonic acids:
- (1) Hydrophobic group joined directly to sulfonated aromatic nucleus (subclasses on basis of nature of hydrophobic group. Alkyl phenols, terpene, and rosin-aromatic condensates, alkyl aromatic ketones, etc.).
- (2) Hydrophobic group joined to sulfonated aromatic nucleus through as intermediate linkage.
- (a) Ester linkage (sulfophthalates, sulfobenzoates).
- (b) Amide and imide linkages.
- (1)  $\text{R}-\text{CONH}-\text{ArSO}_3\text{H}$  type.
- (2) Sulfobenzamide type.
- (c) Ether linkage (alkyl phenyl ether type).
- (d) Heterocyclic linkage (Ultravon type, etc.).
- (e) Miscellaneous and two or more links.
- (E) Miscellaneous anionic hydrophilic groups:
- (1) Phosphages and phosphonic acids.
- (2) Persulfates, thiosulfates, etc.
- (3) Sulfonamides.
- (4) Sulfamic acids, etc.

### II. Cationic

- (A) Amine salts (primary, secondary, and tertiary amines):
- (1) Amino group joined directly to hydrophobic group.
- (a) Aliphatic and aromatic amino groups.
- (b) Amino group is part of a heterocycle (alkaltery type).
- (2) Amino group joined through an intermediate link.
- (a) Ester link.
- (b) Amide link.
- (c) Ether link.
- (d) Miscellaneous links.
- (B) Quaternary ammonium compounds:
- (1) Nitrogen joined directly to hydrophilic group.
- (2) Nitrogen joined through an intermediate link.
- (a) Ester link.
- (b) Amide link.
- (c) Ether link.
- (d) Miscellaneous links.
- (C) Other nitrogenous bases:
- (1) Non-quaternary bases (classified as guanidine, thiuronium salts, etc.).
- (2) Quaternary bases.
- (D) Non-nitrogenous bases:
- (1) Phosphonium compounds.
- (2) Sulfonium compounds, etc.

### III. Non-ionic

- (A) Ether linkage to solubilizing groups.
- (B) Ester linkage.
- (C) Amide linkage.
- (D) Miscellaneous linkages.
- (E) Multiple linkages.

### IV. Ampholytic

- (A) Amino and carboxy:
- (1) Non-quaternary.
- (2) Quaternary.
- 5 (B) Amino and sulfuric ester:
- (1) Non-quaternary.
- (2) Quaternary.
- (C) Amine and alkane sulfonic acid.
- (D) Amine and aromatic sulfonic acid.
- 10 (E) Miscellaneous combinations of basic and acidic groups.

The breaker-absorber employed herein can be any solid material which will maintain its solid form during treatment and is capable of breaking the emulsion and absorbing the outer water-type phase.

In general, these materials are water-absorbing or hydrophilic solids insoluble in either phase.

Non-limiting examples include argillaceous earth or clayey materials, for example, montmorillonite, bentonite, silica, calcium sulfate, aluminum silicate, etc. In addition, water absorbant high surface fibers such as cellulose, asbestos, rockwool, etc. can be employed. Other insoluble hydrate-forming salts can be employed. Any suitable method of treating can be employed—for example, a slurry, a fixed bed, combinations thereof, etc.

The amount of breaker-absorber employed will vary depending on many factors, for example, on particle size, hydrophilic properties, the amount of water in the emulsion, contact time, rate of stirring, etc. With an emulsion containing about 10% or less water preferably having about 5% or less water and employing a clay, such as montmorillonite clay, I employ, for example, at least about 0.25 g./100 ml. of emulsion, for example about 0.3 to 3.0 g., such as about 0.25 to 1.5 g., but preferably about .5 to 1.0 g.

The particle size of the hydrophilic material, for example montmorillonite clay can also vary widely, for example, one having a particle size of about  $1\mu$  to  $10,000\mu$  or greater, such as  $1\mu$  to  $1000\mu$ , but preferably  $5\mu$  to  $500\mu$ .

In order to make the breaker-absorber more effective, it is preferable to employ as little water as possible consistent with producing a satisfactory emulsion, for example less than about 10% water, such as less than about 8% water, for example less than about 5%, but preferably less than about 5% water, such as 5–2% water. In certain instances, where it is desirable, higher ratios of water may be employed such as 20% or more of water.

In general, demulsification is effected by intimately mixing the solid breaker-absorber with the emulsified fuel and then separating the solid breaker-absorber from the fuel. Fast high shear mixing also assists in breaking the emulsion. The product is a clean fuel which meets military specifications.

### Examples

The following examples are presented for purpose of illustration and not of limitation. The system employed is presented in the flow sheet in the drawing where P in the drawing represents pressure.

The smooth, white, highly thixotropic O/W emulsion prepared as in Example 1 of S.N. 411,103 from about 96–97% kerosene and about 3–4% water, by volume, employing n-decanol+PrO(1.96)+EtO(2.61) as an emulsifier, ( ) indicates weights of oxides based on weight of n-decanol, was fed to the demulsification system at the rate of about 1800 ml./minute. A kerosene slurry of montmorillonite-type clay (particle-size  $50\mu$ ) was employed (1.5 g. of clay/100 ml. of kerosene) and added at a rate so that 1 g. of clay treated 100 ml. of fuel emulsion. The clay filtered easily so as to yield a clear fuel which meets military specification.

To save repetitive details the treatment of other emulsified fuels, similarly demulsified is presented in the following table.

TABLE I

Ex.	Emulsion Prepared According to S.N.	Demulsifier-Dehydrator, l. g/100 ml. Kerosene	Ratio (g.) of Active Solids to ml. Emulsion	Comment
1	Ex. 77 of 286,877 <sup>1</sup>	Fullers Earth 50 $\mu$	1/100	Breaks and filters clean. Meets military specifications.
2	do <sup>1</sup>	Synthetic Calcium Silicate 1 $\mu$	1/100	Do.
3	do <sup>1</sup>	Bentonite 200 $\mu$	1/100	Do.
4	do <sup>1</sup>	Anhydrous CaSO <sub>4</sub> 1000 $\mu$	1/100	Do.

<sup>1</sup> An oil-in-water emulsion containing 98% kerosene and 2% water, was made employing an emulsifier prepared from crude alkylphenol foos oxyethylated with 1.75 parts by weight of oxide per part of foos. This application is now abandoned.

The above examples are illustrative of this invention. Other thixotropic emulsions described in the above application are also broken in a similar manner to yield fuels which meet military specifications. For example, the emulsions prepared in Table I of S.N. 411,103 are similarly broken.

As is quite evident, other breaker-absorbers besides those specifically mentioned herein can be employed in my invention. It is, therefore, not only impossible to attempt a comprehensive catalogue of such compositions, but to attempt to describe the invention in its broader aspects in terms of specific chemical names would be too voluminous and unnecessary since one skilled in the art could by following the description of the invention herein select a useful breaker-absorber. This invention lies in the use of suitable breaker-absorbers and their individual compositions are important only in the sense that their properties can affect this function. To precisely define each specific useful breaker-absorber in light of the present disclosure would merely call for chemical knowledge within the skill of the art in a manner analogous to a mechanical engineer who prescribes in the construction of a machine the proper materials and the proper dimensions thereof. From the description in this specification and with the knowledge of a chemist, one will know or deduce with confidence the applicability of specific breaker-absorbers suitable for this invention by applying them in the process set forth herein. In analogy to the case of a machine, wherein the use of certain materials of construction or dimensions of parts would lead to no practical useful result, various materials will be rejected as inapplicable where others would be operative. One can obviously assume that no one will wish to use a useless breaker-absorber, nor will be misled because it is possible to misapply the teachings of the present disclosure to do so. Thus any breaker-absorber that can perform the function stated herein can be employed.

The thixotropic emulsions of this invention described in the above applications are particularly useful in commercial and military operations. For example, when placed in fuel receptacles such as storage tanks, portable fuel receptacles, aircraft, rocket or jet fuel tanks, etc., they are less susceptible to fire or explosion on crashes, under firepower or other igniting conditions, thus resulting in a great saving of life and property.

Thus, any of the unique thixotropic emulsions prepared herein, for example, those in Example 1 of S.N. 411,103, Example 77 of S.N. 286,877, now abandoned, and others described in the applications incorporated by reference into this application, when contained in such receptacles on the ground or in the air are useful in preventing fire and explosions.

Having thus described my invention what I claim as new and desire to obtain by Letters Patent is:

1. A process of resolving a jet and rocket thixotropic hydrocarbon-in-water emulsion fuel comprising (1) water, (2) an emulsifiable hydrocarbon, and (3) an emulsifying agent, said hydrocarbon being present in said emulsion fuel in an amount of at least 80% hydrocarbon by volume of the emulsion, said emulsion having the characteristics of a solid fuel when at rest and the characteristics of a liquid fuel when a force is exerted on it, said emulsion tending to be nonadhesive, said emulsion having a critical shear point sufficient to permit pumping at high rates, and said emulsion having an apparent rest viscosity greater than about 1000 cps., which is characterized by contacting said emulsion with a substantially insoluble breaker-absorber which is capable of interacting with the water phase so as to break the emulsion.

2. The process of claim 1 wherein said hydrocarbon is present in said emulsion in an amount of at least 90% by volume of said emulsion.

3. The process of claim 1 where the breaker-absorber is a clayey material.

4. The process of claim 3 where the breaker-absorber is a montmorillonite-type clay.

5. The process of claim 1 where the breaker-absorber is a hydrate-forming material.

6. The process of claim 3 wherein said hydrocarbon is present in said emulsion in an amount of at least 90% by volume of said emulsion.

7. The process of claim 4 wherein said hydrocarbon is present in said emulsion in an amount of at least 90% by volume of said emulsion.

8. The process of claim 5 wherein said hydrocarbon is present in said emulsion in an amount of at least 90% by volume of said emulsion.

#### References Cited

##### UNITED STATES PATENTS

1,911,797	5/1933	Brown et al.	252-324
1,911,839	5/1933	Meinzer	252-322
1,974,692	9/1934	Robinson	252-324
2,522,378	9/1950	Kirkbride	252-324
3,085,068	4/1963	Hippen	252-324 X
3,242,097	3/1966	Crawford	252-324 X

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