PROCESS FOR BREAKING PETROLEUM EMULSIONS EMPLOYING CERTAIN OXYALKYLATED TRIETHYLENE TETRAMINES

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INVENTOR

Woodrow J. Dickson

INVENTOR
This invention relates to processes or procedures particularly adapted for preventing, breaking or resolving emulsions of the water-in-oil type, and particularly petroleum emulsions. My invention provides an economical and rapid process for resolving petroleum emulsions of the water-in-oil type that are commonly referred to as "cut oil," "frolly oil," "emulsified oil," etc., and which comprise either mineral oils or lubricating oils, or relavtively soft or weak brines. Controlled emulsification and subsequent demulsification under the conditions just mentioned are of significant value in removing impurities particularly inorganic salts, from pipeline oil.

More specifically, the present invention is concerned with a process for breaking petroleum emulsions employing a demulsifier including a cogenic mixture of a homologous series of glycol ethers of triethylene tetramine. The cogenic mixture is derived exclusively from triethylene tetramine, propylene oxide and ethylene oxide in such weight proportions so that the average composition of said cogenic mixture stated in terms of initial reactants lies approximately within the trapezoid of the accompanying drawing in which the minimum triethylene tetramine content is at least 75% and which trapezoid is identified by the fact that its area lies within the straight lines connecting A, B, F, E. My preference by far is to use the compositions which represent less than one-half of this total area, to wit, the smaller trapezoid A, B, D, C.

It is immaterial as to whether one reacts the amine with propylene oxide first and then with ethylene oxide, or with ethylene oxide and then with propylene oxide; or, for that matter, one may employ a mixture of the two oxides; or if desired, one may add a small amount of ethylene oxide, then propylene oxide, and then more ethylene oxide.

Referring to the hereto attached drawing it is simplified by noting that one may react triethylene tetramine with enough ethylene oxide so the binary reaction product falls within the mixture identified by the line CC-DE on the extremity of the graph which shows combinations derived solely from triethylene tetramine and ethylene oxide. After obtaining such binary reaction product it can then be reacted with propylene oxide so as to bring it within the area of the trapezoid A, B, E, F, or preferably within the smaller trapezoid A, B, D, C.

Similarly, one can produce a binary reaction product from triethylene tetramine and propylene oxide as identified by the comparable line AA—BB and subject this reaction product to oxycylation so as to bring the composition within the area of the trapezoid and preferably within the area of the small trapezoid A, B, D, C.

For the purpose of resolving petroleum emulsions of the water-in-oil type, I prefer to employ oxycylated derivatives, which are obtained by the use of monoxides, in such manner that the derivatives so obtained have sufficient hydrophilic character to meet at least the test set forth in U. S. Patent No. 2,499,368, dated March 7, 1950, to Ge Groote and Keizer. In said patent such test for emulsification using a water-insoluble solvent, generally xylene, is described as an index, of surface activity.

The above mentioned test, i.e., a conventional emulsification test, simply means that the preferred product for demulsification is soluble in a solvent having hydrophobe properties or in an oxygenated water insoluble solvent, or even in a mixture containing a fraction of a water-soluble oxygenated hydrocarbon solvent and that when shaken with water the product may remain in the non-aqueous solvent or, for that matter, it may pass into the aqueous solvent. In other words, although it is xylene soluble, for example, it may also be water soluble to an equal or greater degree.

For purposes of convenience, what is said hereinafter will be divided into three parts:

Part 1 is concerned with the oxycylation of triethylene tetramine in a general way;

Part 2 is concerned with the oxycylation of triethylene tetramine using two different oxides, i.e., propylene oxide and ethylene oxide so as to produce derivatives falling within said compositional limits as previously described and noted hereinafter in detail;

Part 3 is concerned with the resolution of petroleum emulsions of the water-in-oil type by means of the previously described chemical compounds.

PART 1

The oxycylation of amines is well known. This applies particularly to reactions involving monoxides having not over 4 carbon atoms, such as ethylene oxide and propylene oxide. As to the oxycylation of a mono-amine such as cyclohexylamine, see U. S. Patent No. 2,626,922, dated January 27, 1955, to De Groote. As to the oxycylation of a polyamine, see U. S. Patents Nos. 2,592,530, 2,552,531 and 2,552,534, all dated May 15, 1951, and all to De Groote.

The oxycylation of an amine is comparable to other well known oxycylations and under certain conditions may require variation. There is no problem if the amine is a liquid or if it is xylene-soluble or soluble in an equivalent solvent, or can be melted and reacted at the melting point. In the case of triethylene tetramine the product is a liquid and the procedure is comparatively simple. However, the most satisfactory procedure in event of a solid is to use a slurry of the finely powdered material in xylene comparable to the oxycylation of sorbitol. As to this procedure, see Example A in U. S. Patent No. 2,552,528, dated May 15, 1951, to De Groote.

The oxycylation of triethylenetetramine is comparable to the oxycylation of a liquid such as triethanolamine. Oxycylation generally takes place readily at the usual oxycylation temperatures for instance 110° C. to 150° C. However, in the initial exhaustive oxycylation of any product it is usually desirable to use a minimum amount of the product so that considerable oxide can be added. This prevents the production of an effective stirring at the early stages. For this reason it is convenient to add an inert solvent, such as xylene or a high boiling aromatic petroleum solvent, without differentiating whether one obtains a solution or a slurry, or in the case of a liquid, a suspension or temporary emulsion.

In due course oxycylated derivatives of the kind herein described produce products which are soluble in either xylene or high boiling aromatic petroleum solvents. For this rea-
son what is said herein elsewhere refers to the oxyalkyla-
tion as if it occurred at ordinary temperatures but even a solid at the oxyalkylation tem-
perature. If, in fact, it happened to be a liquid, and preferably a solvent-soluble liquid at oxyalkylation tem-
perature, so much the better.

In order to illustrate why the herein contemplated compound, or said products are cogenic mixtures and not single chemical compounds, and why they must be
described in terms of manufacture, and molar ratio or
percentage ratio of reactants, reference is made to a
monohydric alcohol. Triethylene tetramine has 6 rea-
tive hydrogen atoms and thus at the beginning or early
stage of oxyalkylation, it becomes obvious that one is really
producing a polymer of the alkylene oxide except
for the terminal group. This is particularly true where
the amount of oxide added is comparatively large, for
instance, 10, 20, 30, 40, or 50 units. If such a compound is
subjected to oxyalkylation so as to introduce 30 units
of ethylene oxide, it is well known that one does not
obtain a single constituent which, for sake of conver-
sion, may be indicated as \( RO(CH_2)_{30}OH \). Instead, one
obtains a cogenic mixture of closely related homologous
compounds in which the formula may be shown as the
following: \( RO(CH_2)_nH \), wherein \( n \), as far as the
statistical average goes, is 30, but the individual members
present in significant amount may vary from instance
to instance, where \( n \) has a value of 25 and perhaps less, to a point
where \( n \) may represent 35 or more. Such mixture is, as
stated, a cogenic closely related series of touching ho-
mologous compounds. Considerable investigation has
been made in regard to the distribution curves for linear
polymers. Attention is directed to the article entitled
"Fundamental Principles of Condensation Polymeriza-
tion," by Paul J. Flory, which appeared in Chemical
Reviews, Volume 39, No. 1, page 137.

Unfortunately, as has been pointed out by Flory and
other investigators, there is no satisfactory method, based
on either experimental or mathematical examination, of
indicating the exact proportion of the various members
of touching homologous series which appear in cogenic
condensation products of the kind described. This means
that from the practical standpoint, i.e., the ability to
describe how to make the product under consideration and
how to repeat such production time after time without
difficulty, it is necessary to resort to some other method
of description.

What has been said in regard to a monohydric com-
 pound of course is multiplied many times in the case of a
 compound such as triethylene tetramine.

Although acid catalysts are used in oxyalkylations they
are used to a lesser extent in the oxyalkylations of basic
amines and the like. Under said circumstances one may
have to use enough of the acid catalyst to neutralize the
basicity of the product and convert it into a salt. This is
not true where certain clays or prepared earths are used
which act as acidic catalysts. In any event, it is our
preference to use basic catalysts such as caustic soda,
sodium methylete, or the like.

**PART 2**

The oxyalkylation of an amine, particularly a primary
amine, or secondary amine or a hydroxylated amine
regardless of whether it is primary, secondary, or tertiary,
is comparatively simple and has been described repeatedly
in the literature.

If the product is a liquid, such as triethanolamine, one
can proceed to treat with an alkylene oxide such as ethyl-
ene oxide, propylene oxide, or butylene oxide, at least in
the early stages if desired without adding any catalyst.
Generally speaking, if oxyalkylation is rather extensive
in the present instance, one requires a catalyst after
the initial stage and it is just as simple to add it from the
very beginning.

The oxypropylation of a polylamine, such as triethylene
tetramine, is comparatively simple because such products
or similar products are usually liquids at ordinary tem-
perature and invariably at oxyalkylation temperatures.
Indeed, the procedure is simply to oxyalkylate without ad-
dition of any catalyst if desired and then when oxyalkyla-
tion slows up add the usual basic catalyst, such as pow-
dered caustic soda or powdered sodium methylete.
If desired, such catalyst can be added at the very
beginning.

It is also desirable in such cases where exhaustive oxy-
alkylation is concerned to add a diluent, such as xylene,
high boiling petroleum solvent, or the like, at the very
beginning. Such solvents usually are miscible but if
not miscible one obtains a suspension or temporary emul-
sion and as soon as oxyalkylation has proceeded to even
a slight degree the entire mass becomes homogeneous.

Specific reference is made to the instant application
which is concerned with ethylene oxide and propylene
oxide or the equivalents. Actually, whether one uses
ethylene oxide or propylene oxide or, for that matter,
butylene oxide, one preferably starts with a polylamine
suspended in the form of a slurry, an emulsion, a suspensa
on or as a solution. There would be a slurry in event
the amine is a solid and insoluble. In the present case,
however, the amine is a liquid as pointed out.

If desired, one can employ an alkylene carbonate, such
as ethylene carbonate, butylene carbonate, or propylene
carbonate, for the initial oxyalkylation. Where such
initial oxyalkylation has gone far enough to convert the
polylamine into a solvent-soluble product, i.e., soluble
in xylene or an aromatic petroleum solvent, one can then
use the oxides. The carbonates, of course, cost more
than the oxides and there is no real advantage in most
cases unless one starts with an insoluble amine such as
tris-(hydroxymethyl)aminomethane and this does not apply
in the present case.

In any event, as is well known the oxyalkylation of polylamines proceeds as readily as the oxyalkylation
and this applies also to oxybutylation, particularly if the
straight chain butylene oxide isomers are employed. See,
for example, U. S. Patents Nos. 2,679,511, 2,679,512,
2,679,515, 2,679,514, and 2,679,515, all dated May 25,
1954, to De Groote.

It is not believed any examples are necessary to illus-
trate such well known procedure but for purposes of illus-
tration the following are included:

**Example 1a**

The reaction vessel employed was a stainless steel auto-
clave with the usual devices for heating, heat control,
stirrer, inlet, outlet, etc., which is conventional in this
type of apparatus. The capacity was approximately 4
liters. The stirrer was operated at a speed of approxim-
ately 250 R. P. M. There were charged into the auto-
clave 500 grams of triethylene tetramine, 300 grams of
xylene, and 15 grams of sodium methylete. The auto-
clave was sealed, swept with nitrogen gas and stirring
started immediately and heat applied. The temperature
was allowed to rise to approximately 155° C. At this
particular time the addition of propylene oxide was
started. Propylene oxide was added continuously at such
speed that it was absorbed by the reaction as added. The
amount added in this operation was 1500 grams. The
time required to add the propylene oxide was two hours.
During this period the temperature was maintained at 140° to 155° C., using cooling water through the inner coils when necessary and otherwise applying heat if required. The maximum pressure during the reaction was 50 pounds per square inch. Ignoring the xylene and sodium methylene and considering only the triethylene tetramine for convenience, the resultant product represents 3 parts by weight of propylene oxide to one part by weight of triethylene tetramine. The xylene present represented approximately 6 parts by weight.

Example 2aa

The reaction mass of Example 1aa was transferred to a larger autoclave (capacity 15 liters). Without adding any more solvent or any more xylene the procedure was repeated so as to add another 1500 grams of propylene oxide under substantially the same operating conditions but requiring about 3 hours for the addition. At the end of this step the ratio represented approximately 6 to 1 (ratio propylene oxide to triethylene tetramine).

Example 3aa

In a third step, instead of adding 1500 grams of propylene oxide to the product of Example 1aa, 1625 grams were added. The reaction slowed up and required approximately 6 hours, using the same operating temperatures and pressures. The ratio at the end of the third step was 9.25 parts by weight of propylene oxide per weight of triethylene tetramine.

Example 4aa

At the end of the third step (Example 3aa) the autoclave was opened and an additional 5 grams of sodium methylene added, the autoclave flushed out as before, and the fourth and final oxalylalkylation completed, using 1625 grams of propylene oxide, and the oxalylalkylation was complete within 3% hours using the same temperature range and pressure as previously. At the end of the reaction the product represented approximately 12.5 parts of propylene oxide by weight to one part of triethylene tetramine.

Having obtained oxypropylated triethylene tetramine the products were subjected to oxyethyllylation in a manner comparable to the oxyxlylation of triethanolamine, or for that matter, in the same way that oxypropylated sucrose is subjected to oxyethyllylation in the manner described in U. S. Patent No. 2,652,394, dated September 15, 1953, to De Grootc. Indeed, the procedure is comparatively simple for the reason that one is working with a liquid and also that ethylene oxide is more reactive than propylene oxide. As a result, using the same amount of catalyst one can oxyethyllylate more rapidly and usually at a lower pressure.

The same procedure using triethylene tetramine in xylene was employed in connection with ethylene oxide and the same mixture on a percentage basis was obtained as in the above examples where propylene oxide and triethylene tetramine were used.

In the preceding procedures one oxide has been added and then the other. One need not follow this procedure. The two oxides can be mixed together in suitable proportions and subsequently subjected to point oxalylalkylation so as to obtain products coming within the specified limits. In such instances, of course, the oxalylalkylation may be described as random oxalylalkylation insofar that one cannot determine the exact location of the propylene oxide or ethylene oxide groups. In such instances the procedure again is identical with the same as previously described and, as a matter of fact, I have used such methods in connection with triethylene tetramine.

Actually, triethylene tetramine at times may contain a trace of moisture. My preference is to prepare the solution with an excess of xylene and distill off a part of the xylene so as to remove any trace of water and then flush out the mass with nitrogen. Even so, there may be a few tenths of a percent of moisture remain although at times examination indicates at the most it is merely a trace.

As previously pointed out the simplest procedure of all is to prepare a binary reaction product of triethylene tetramine and ethylene oxide on the one hand or triethylene tetramine and propylene oxide on the other hand, and react with the other oxide. Note line CC-DD which indicates that in the binary reaction product obtained from triethylene tetramine and ethylene oxide one employs approximately 66.6% to 96.5% of ethylene oxide and approximately 3.5% to 33.4% of triethylene tetramine.

Similarly, if one refers to the line AA—BB it means one would employ from 1.95% of triethylene tetramine up to 14.3% of triethylene tetramine and from 85.7% of propylene oxide up to 98.05% of propylene oxide.

In other operations I have proceeded to do as follows: Mixed the triethylene tetramine with an aromatic petroleum solvent and with powdered caustic soda. I have stirred this mixture at 125° to 130° C. for a short period of time, approximately one-half hour, flushed out with nitrogen, and then subjected to vacuum so as to eliminate any moisture. I then started to oxypropylene and continued until oxypropylation was complete and then immediately followed with ethylene oxide. In these examples the amounts of materials used are indicated in pounds, and in each instance, of course, a suitable size autoclave was used. Although the oxalylalkylation started under vacuum the maximum pressure at any time was about 10 to 15 pounds. An efficient agitating device was used and stirring speed was approximately 350 R. P. M.

These data covering nine oxalylalkylations are included in Table I, immediately following. The time periods are shown. Incidentally, I have repeated these same operations using ethylene oxide first and then propylene oxide and I have also mixed the two oxides and completed the same nine oxalylalkylations under substantially the same conditions.

### Table I

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>1a.</td>
<td>10.0</td>
<td>8.47</td>
<td>1.3</td>
<td>109.0</td>
<td>40.5</td>
<td>10.5</td>
<td>125-130</td>
<td>10-15</td>
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<tr>
<td>1b.</td>
<td>7.4</td>
<td>9.25</td>
<td>1.07</td>
<td>109.0</td>
<td>40.5</td>
<td>10.5</td>
<td>125-130</td>
<td>10-15</td>
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<tr>
<td>2a.</td>
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<td>7.92</td>
<td>1.66</td>
<td>104.0</td>
<td>42.5</td>
<td>10.5</td>
<td>125-130</td>
<td>10-15</td>
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<td>6.28</td>
<td>8.32</td>
<td>1.0</td>
<td>101.1</td>
<td>31.4</td>
<td>12.0</td>
<td>125-130</td>
<td>10-15</td>
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<tr>
<td>3a.</td>
<td>2.0</td>
<td>1.73</td>
<td>9.5</td>
<td>123.5</td>
<td>5.5</td>
<td>12.0</td>
<td>125-130</td>
<td>10-15</td>
</tr>
<tr>
<td>3b.</td>
<td>3.65</td>
<td>9.02</td>
<td>1.0</td>
<td>115.0</td>
<td>36.5</td>
<td>12.0</td>
<td>125-130</td>
<td>10-15</td>
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<tr>
<td>4a.</td>
<td>1.8</td>
<td>3.3</td>
<td>5.0</td>
<td>101.0</td>
<td>6.5</td>
<td>12.0</td>
<td>125-130</td>
<td>10-15</td>
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<tr>
<td>4b.</td>
<td>1.87</td>
<td>4.19</td>
<td>1.1</td>
<td>125.8</td>
<td>6.0</td>
<td>12.0</td>
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<tr>
<td>5a.</td>
<td>1.06</td>
<td>.9</td>
<td>.6</td>
<td>40.0</td>
<td>12.6</td>
<td>4.0</td>
<td>125-130</td>
<td>10-15</td>
</tr>
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</table>
Referring again to the ratio of the initial reactants based on the trapezoid in attached drawing, I have calculated the percentages of the two initial reactants for the points A, B, C, D, E, and F and Nos. 1 through 14, inclusive. I have also calculated initial binary mixtures corresponding in essence to the lines CC—DD and AA—BB, all of which appears in self-explanatory form in Table II, immediately following.

### Table II

<table>
<thead>
<tr>
<th>Points on boundary of area</th>
<th>Tertiary mixture, percent basis</th>
<th>Binary intermediate mixtures, percent basis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Di-ethylene tetramine</td>
<td>Propylene oxide</td>
</tr>
<tr>
<td>A</td>
<td>1.75</td>
<td>38.25</td>
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<tr>
<td>B</td>
<td>7.50</td>
<td>50.00</td>
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<tr>
<td>C</td>
<td>15.8</td>
<td>75.50</td>
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<tr>
<td>D</td>
<td>10.0</td>
<td>70.00</td>
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<tr>
<td>E</td>
<td>10.0</td>
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<td>F</td>
<td>7.82</td>
<td>76.40</td>
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<td>G</td>
<td>7.62</td>
<td>78.30</td>
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<td>H</td>
<td>7.82</td>
<td>76.40</td>
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<tr>
<td>I</td>
<td>7.70</td>
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<td>J</td>
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<tr>
<td>O</td>
<td>7.70</td>
<td>78.10</td>
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</table>

As previously pointed out, the oxalkylation of triethylene tetramine or similar hydroxylated mono- or polyamines has been described in the literature and is described also in detail above. All one need do is employ such conventional oxalkylation procedure to obtain products corresponding to the compositions as defined. Attention is again directed to the fact that one need not add the entire amount of ethylene oxide at one time but that a small portion of one could be added and then another small portion of the other, and the process repeated.

For purpose of illustration I have prepared examples in three different ways corresponding to the compositions on the drawing. In the first series propylene oxide and ethylene oxide were mixed; this series is indicated as Ac, Bc, etc., through and including 14a; in the second series propylene oxide was used first followed by ethylene oxide and this series is indicated as Ab, Bc, etc., through and including 14g; and finally in a third series, ethylene oxide was used first followed by propylene oxide and this series is indicated as Ac, Bc, etc., through and including 14g. This relationship is shown in Table III.

### Table III

<table>
<thead>
<tr>
<th>Composition corresponding to following point</th>
<th>Composition where oxides are mixed prior to oxalkylation</th>
<th>Composition where propylene oxide used first followed by ethylene oxide</th>
<th>Composition where ethylene oxide used first followed by propylene oxide</th>
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<tbody>
<tr>
<td>A</td>
<td>Ac</td>
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<td>Ac</td>
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<td>B</td>
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</table>

The products obtained by the above procedure usually show some color varying from a light amber to a pale straw. They can be bleached in the usual fashion using bleaching clays, carbon, or an organic bleach, such as peroxide or peracetic acid, or the like.

There are certain variants which can be employed without detracting from the metes and bounds of the invention, but for all practical purposes there is nothing to be gained by such variants and the result is merely increased cost. For instance, any one of the two oxides can be replaced to a minor percentage and usually to a very small degree, by oxide which would introduce substantially the same group along with a side chain, for instance, one could employ glycidy methyl ether, glycydyl ethyl ether, glycidyl isopropyl ether, glycydyl butyl ether or the like.

Increased branching also may be effected by the use of an imine instead of a glycidyl, or a methyl glycidyl. Thus one can use ethylene imine, or propylene imine in the same way described for glycidyl or methyl glycidyl. An additional effect is obtained due to the basicity of the nitrogen atom. The same thing is true as far as the inclusion of nitrogen atoms if one uses a compound of the kind previously described such as a dialkylaminooxypropane. Excellent products are obtained by reacting triethylene tetramine with 1 to 5 moles of ethylenic imine and then proceeding in the same manner herein described.

In the hereinafter appended claims reference has been made to "glycol ethers of triethylene tetramine." Actually it well may be that the products should be referred to as "polyol ethers of triethylene tetranine" in order to emphasize the fact that the final products of reaction have more than two hydroxyl radicals. However, the products may be considered as hypothetically derived by condensation of triethylene tetramine with the glycols, such as ethylene glycol, butylene glycol, propylene glycol, or polyglycols. For this reason there seems to be a preference to use the terminology "glycol ethers of triethylene tetramine."

In a trapezoid such as A, B, D, C, the area can be divided conveniently into five portions by first drawing two lines from the shorter of the two parallel sides perpendicular so as to intersect the other longer parallel line in two places, thus dividing the trapezoid into two triangles and a rectangle. The rectangle then obviously can be divided into three portions of the same size by drawing two additional lines, all of which is shown in the drawing on a larger scale and in dotted lines only. In the hereinafter attached claims the area within the upper apex of the trapezoid refers to the area within such upper triangle; the area within the lower apex of the trapezoidal area...
refers to such lower triangle. The area in the center of the trapezoid refers to the area defined by the middle rectangle. The area of one rectangle is defined by being between the upper apex and the center rectangle, and the other by being between the lower apex and the center rectangle, all of which is perfectly plain by reference to the drawing. An attempt to draw additional lines and to number them in the same trapezoid A, B, D, C, would only tend towards confusion and thus the present means is being employed to point out the various areas which, in turn, appear in the sub-paragraph claims hereto appended.

Thus in the drawing, the area designated V corresponds to the area within the upper triangle, the area W corresponds to the area within the lower triangle, the area X corresponds to that of the middle triangle, and the areas Y and Z correspond to those of the other rectangles.

PART 3

As to the use of conventional demulsifying agents reference is made to U.S. Patent No. 2,626,029, dated January 27, 1953, to De Groote, and particularly to Part 3. Everything that appears therein applies with equal force and effect to the instant concept, noting only that where reference is made to Example 159 in said text beginning in column 13, line 20, reference should be to Example 58 herein described.

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

1. A process for breaking petroleum emulsions of the water-in-oil type characterized by subjecting the emulsion to a demulsifying agent including a cogeneric mixture of a homologous series of glycol ethers of triethylene tetramine; said cogeneric mixture being derived exclusively from triethylene tetramine, propylene oxide and ethylene oxide in such weight proportion so the average composition of said cogeneric mixture stated in terms of the initial reactants lies approximately within the trapezoid of the accompanying drawing in which the minimum triethylene tetramine content is at least 1.75% and which trapezoid is identified by the fact that its area lies within the straight lines A, B, E, F, G, H, I, J, K, L, M, N, O, P, Q, R, S, T, U, V, W, X, Y, Z, and that at least part of the propylene oxide is added first.

2. The process of claim 1 with the proviso that oxyalkylation takes place in presence of an alkaline catalyst.

3. The process of claim 1 with the proviso that oxyalkylation takes place in presence of an alkaline catalyst and that at least part of the propylene oxide is added first.

4. The process of claim 1 with the proviso that oxyalkylation takes place in presence of an alkaline catalyst and that all the propylene oxide is added first.

5. A process for breaking petroleum emulsions of the water-in-oil type characterized by subjecting the emulsion to a demulsifying agent including a cogeneric mixture of a homologous series of glycol ethers of triethylene tetramine; said cogeneric mixture being derived exclusively from triethylene tetramine, propylene oxide and ethylene oxide in such weight proportion so the average composition of said cogeneric mixture stated in terms of initial reactants lies approximately within the trapezoid of the accompanying drawing in which the minimum triethylene tetramine content is at least 1.75% and which trapezoid is identified by the fact that its area lies within the straight lines A, B, D, C; with the proviso that all the propylene oxide is added first in the presence of an alkaline catalyst.

6. The process of claim 5 with the proviso that the reactant composition approximates a point in the area corresponding with Y within the upper apex of the trapezoid A, B, D, C.

7. The process of claim 5 with the proviso that the reactant composition approximates a point in the area corresponding with W within the lower apex of the trapezoid A, B, D, C.

8. The process of claim 5 with the proviso that the reactant composition approximates a point in the area corresponding with X of the central part of the trapezoid A, B, D, C.

9. The process of claim 5 with the proviso that the reactant composition approximates a point in the area corresponding with Y between the central part of the trapezoid A, B, C, D, and the upper apex.

10. The process of claim 5 with the proviso that the reactant composition approximates a point in the area corresponding with Z between the central part of the trapezoid A, B, D, C, and the lower apex.

11. A process for breaking petroleum emulsions of the water-in-oil type characterized by subjecting the emulsion to a demulsifying agent including a cogeneric mixture of a homologous series of glycol ethers of triethylene tetramine; said cogeneric mixture being derived exclusively from triethylene tetramine, propylene oxide and ethylene oxide in such weight proportion so the average composition of said cogeneric mixture stated in terms of the initial reactants lies approximately within the trapezoid of the accompanying drawing in which the minimum triethylene tetramine content is at least 1.75% and which trapezoid is identified by the fact that its area lies within the straight lines A, B, F, E; with the proviso that the hydrophile properties of said cogeneric mixture in an equal weight of xylene are sufficient to produce an emulsion when said xylene solution is shaken vigorously with one to three volumes of water.

12. The process of claim 11 with the proviso that oxyalkylation takes place in presence of an alkaline catalyst.

13. The process of claim 11 with the proviso that oxyalkylation takes place in presence of an alkaline catalyst and that all the propylene oxide is added first.

14. The process of claim 11 with the proviso that oxyalkylation takes place in presence of an alkaline catalyst and that all the propylene oxide is added first.

15. A process for breaking petroleum emulsions of the water-in-oil type characterized by subjecting the emulsion to a demulsifying agent including a cogeneric mixture of a homologous series of glycol ethers of triethylene tetramine; said cogeneric mixture being derived exclusively from triethylene tetramine, propylene oxide and ethylene oxide in such weight proportion so the average composition of said cogeneric mixture stated in terms of initial reactants lies approximately within the trapezoid of the accompanying drawing in which the minimum triethylene tetramine content is at least 1.75% and which trapezoid is identified by the fact that its area lies within the straight lines A, B, D, C; with the proviso that all the propylene oxide is added first in the presence of an alkaline catalyst; with the proviso that the hydrophile properties and said cogeneric mixture in an equal weight of xylene are sufficient to produce an emulsion when said xylene solution is shaken vigorously with one to three volumes of water.

16. The process of claim 15 with the proviso that the reactant composition approximates a point in the area corresponding with Y within the upper apex of the trapezoid A, B, D, C.

17. The process of claim 15 with the proviso that the reactant composition approximates a point in the area corresponding with W within the lower apex of the trapezoid A, B, D, C.

18. The process of claim 15 with the proviso that the reactant composition approximates a point in the area corresponding with X of the central part of the trapezoid A, B, D, C.

19. The process of claim 15 with the proviso that the reactant composition approximates a point in the area corresponding with Y between the central part of the trapezoid A, B, D, C, and the upper apex.

20. The process of claim 15 with the proviso that the reactant composition approximates a point in the area.
corresponding with Z between the central part of the trapezoid A, B, D, C, and the lower apex.

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