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3,355,386

GERMICIDAL NONIONIC-DETERGENT  
IODINE COMPOSITIONS

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This invention relates to nonionic detergent-iodine complexes which provide enhanced iodine color in use dilutions, and to germicidal compositions containing such complexes. More particularly, the invention relates to such detergent-iodine complexes wherein a substantial color enhancement is provided by detergent components which are water-soluble condensates of ethylene oxide and a hydroxy compound providing a hydrophobic moiety having an average aliphatic carbon content in the C<sub>12</sub> to C<sub>18</sub> range, and wherein further color enhancement is provided by detergent components having the hydrophobic moiety characterized as above described, but having the ethylene oxide partially replaced or supplemented by propylene oxide.

It has been known for many years that detergent complexed iodine solutions show increased color over aqueous iodine solutions. The differences among detergent classes with respect to iodine color have not been taught, although some of those skilled in the art, may be aware of such differences. The differences in detergent-iodine color within a particular class of detergents is not known, and has never been described before.

Most iodine use dilutions for cleaning purposes are made at the 25 p.p.m. to 75 p.p.m. available iodine level. At these levels the iodine color can readily be seen; differences in color as a function of the detergent, measurable by instrument, can hardly be detected by eye and so have never attracted attention. Dilutions at the 12½ p.p.m. level, used exclusively as a sanitizing rinse, have been only faintly colored. Since such solutions are used on surfaces that are clean to begin with, there is almost no loss of iodine through reaction with proteinaceous soil, and so the problem of viewing the color as a measure of when replenishment is necessary is not of great importance. To the extent that improved color of detergent-iodine use dilutions can extend the range of iodine perception, the amount of iodine necessary in use dilutions for both the cleaning and sanitizing purposes can be safely lowered. This is for the reason that iodine is recognized as germicidally active in concentrations as low as fractions of a p.p.m.

It has been suggested in Shelanski Patent No. 2,931,777 that as the detergent component of germicidal detergent iodine composition there may be employed polyalkylene oxide derivatives of water-insoluble aliphatic hydroxy compounds. It has been found that such detergents vary widely in iodine complexing capacity and in properties of the resulting detergent-iodine compositions with variations in both the hydrophobic and the hydrophilic components. Such variation is in no way suggested by the disclosure of said patent, and in fact, the patent contains no specific disclosure or illustrative examples of compositions in which iodine is complexed with condensates of water-insoluble aliphatic hydroxy compounds and ethylene oxide.

It has been discovered, in accordance with the present invention, that primary aliphatic alcohols having an average carbon content within the C<sub>12</sub> to C<sub>18</sub> range, and preferably within the C<sub>14</sub> to C<sub>18</sub> range will, when condensed with ethylene oxide, provide detergents which can be employed as iodine carriers with superior effec-

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tiveness. Detergents formed from secondary alcohols are distinctly inferior as iodine carriers.

It is therefore an underlying concept of the present invention that the new detergent-iodine compositions contain a detergent in which the hydrophobic moiety is a primary aliphatic alcohol, or primary aliphatic alcohol mixture of the C<sub>12</sub> to C<sub>18</sub>, and preferably the C<sub>14</sub> to C<sub>18</sub> range. In this connection, it is to be understood that such alcohols and the detergents formed therefrom are generally not individual compounds, but mixtures characterized by average carbon atom content. Thus, a commercial C<sub>14</sub> alcohol may itself be a mixture of two, three or more alcohols containing as few as 10 or as many as 20 or more carbon atoms in proportions to average C<sub>14</sub> for the mixture.

Until recently commercial primary aliphatic alcohols were derived from "natural" products containing even numbered fatty acids. Today there are synthetic primary alcohols available which may contain mixtures of odd and even numbered carbon chains, or which may be exclusively even numbered. It has been found that there is no significant difference between even and odd numbered primary aliphatic alcohols as components of detergents used in the present invention.

Where ethylene oxide is condensed with the C<sub>12</sub> to C<sub>18</sub>, and preferably C<sub>14</sub> to C<sub>18</sub> alcohols, the products vary from water insoluble liquids, to water-soluble waxes and solids as the amount of condensed ethylene oxide is increased. Water solubility, and hence suitability for use as iodine carrier, is generally reached when the number of carbon atoms supplied by the ethylene oxide approximately equals or exceeds the number of carbon atoms in the alcohol. Expressed another way, the number of moles of ethylene oxide should be at least

$$\frac{n}{2} - 1$$

with  $n$  being the average number of carbon atoms in the alcohol component. Thus, a C<sub>12</sub> alcohol condensed with 5 or more moles of ethylene oxide and a C<sub>16</sub> alcohol condensed with 7 or more moles of ethylene oxide will generally be water-soluble and suitable for use as an iodine carrier.

In many detergent-iodine preparations, it is preferable that the detergent-iodine complex itself be a liquid, although in special instances, as where a dry, powdered composition is desired, it can be a waxy or solid complex. Furthermore, it is possible, although somewhat more difficult, to prepare aqueous liquid concentrates when using waxy or solid detergents. There is therefore, no well defined upper limit to the amount of ethylene oxide which should be condensed with the alcohol. It should be noted, however, that when liquid complexes are desired, the proportion of ethylene oxide to alcohol becomes quite limited, and progressively more limited as the alcohol contains more carbon atoms. Thus, with a C<sub>12</sub> alcohol, the presence of 20 or more moles of ethylene oxide will generally provide a waxy condensate, whereas with a C<sub>16</sub> and C<sub>18</sub> alcohol, all water-soluble ethylene oxide condensates are of waxy or solid form. It should be noted that ethoxylated mixed primary alcohols may contain substantial amounts of the higher molecular weight alcohols and still provide a water-soluble, liquid condensate; and such mixtures are preferable in most instances to ethoxylated single alcohols.

Just as there is a minimum of EO, about

$$\frac{n}{2} - 1$$

that must be added to a primary alcohol to achieve water solubility, there is a point beyond which the further addition of EO only serves to dilute the chromophoric entity.

In general, this less desirable point is reached when about  $2n-1$  moles of EO have been added. Primary aliphatic alcohols containing  $2n-1$  moles of EO, do not give satisfactory detergent-iodine solution colors at the 6 p.p.m. iodine level unless considerable excesses of detergent are used.

The water-soluble alcohol-ethylene oxide condensates, whether in the form of liquids or waxy solids, can be complexed with iodine by merely mixing together the detergent and elemental iodine at suitably elevated temperatures, i.e., about  $50^{\circ}\text{C}$ . or such higher temperature as is necessary to melt the waxy detergent. When the detergent is a liquid, the complexing can even be effected by room temperature mixing, but the extended time required makes this impractical.

A preferred method of preparing the complexes is the cold mixing process disclosed in United States Patent No. 3,028,299, wherein iodine is supplied as an aqueous iodide-iodine solution suitably containing about 57% by weight  $\text{I}_2$ , 20% HI and the balance water. This method is particularly desirable in preparing iodine complexes with waxy or solid alcohol-ethylene oxide condensates.

The detergent-iodine complexes of the present invention may be employed in germicidal compositions containing amounts of detergent within the range of about 0.5 to 75%, and of available iodine within the range of about 0.1 to 25%. Compositions containing about 1-15% available iodine and 5-75% detergent are suitable for products which can be diluted with water when used by a consumer. Compositions containing from about 15-25% available iodine and about 60-75% detergent can be used as manufacturing concentrates. Compositions in which the available iodine is from about 0.1 to 1.0% containing about 0.5 to 10% detergent may be suitably used directly without dilution with water. In non-acidified products for general environmental sanitation purposes, the remainder of the composition can be water, or a mixture of water and isopropyl-alcohol. On the other hand, for dairy use and other uses encountering excessive amounts of organic soil, it is preferable to employ as added components, a mixture of water with compatible acids.

When compositions are prepared by the cold method using the above mentioned aqueous HI-iodine solution, the composition will also contain about 1 part of  $\text{I}^-$  to each 3 parts of  $\text{I}_2$ . Thus, a composition containing 1.5%  $\text{I}_2$  will contain about 0.5%  $\text{I}^-$ .

An important advantage of the new compositions is the superior built-in indicator provided in typical use dilutions of 25 p.p.m., 12.5 p.p.m., and particularly 6 p.p.m. due to the enhanced color of such solutions. It is the practice to instruct customers using detergent-iodine compositions to discard use dilutions when the characteristic iodine color is gone. With many available compositions, however, the color at dilutions as low as 10 to 15 p.p.m., becomes so faint that end point detection becomes difficult. Such use dilutions are frequently discarded when as much as 50 to 75% of their germicidal activity remains unconsumed. The well established public health utility of decimal p.p.m. concentrations of available iodine further underscores the significance of lowering the threshold of visibility of iodine color. Any sharpening of the end point by providing greater color intensity at the lower use dilutions is also of substantial economic importance in enabling the customer to realize greater sanitizing value from a given amount of detergent-iodine composition.

The enhanced color at use dilutions as low as the 5 to 10 p.p.m. range has been found to be primarily a function of the number of carbon atoms in the primary alcohol which is condensed with ethylene oxide. Best results are obtained with condensates in which the alcohol component has an average of 14 to 18 carbon atoms; and there is a sharp drop-off of color intensity when switching

from condensates derived from  $\text{C}_{12}$  to  $\text{C}_{10}$  primary alcohols.

Secondary alcohols form condensates with ethylene oxide which will complex with iodine, but there is excessive reaction between the iodine and the condensate, with resulting drop in available iodine, which makes such condensates unsatisfactory. In fact, such interreaction is so pronounced when combining with iodine by the normal hot process, that as shown below, a charring results which completely masks the iodine color at low use dilutions, thereby negating this most unique property of germicidal iodine solutions. It is significant that most detergent-iodine manufacturers at this time use the hot process. The inherent instability of secondary alcohol-iodine combinations is such as to make their use questionable even in compositions made under milder conditions where the decomposition takes longer to become evident.

The color enhancing effect of condensates of  $\text{C}_{12}$  to  $\text{C}_{18}$  primary alcohol with ethylene oxide does not appear to be greatly modified by moderate variation in the ethylene oxide content. As previously indicated, the number of carbon atoms provided by the ethylene oxide should be about equal to, or greater than, the number of carbon atoms in the alcohol. The preferred range appears to be about 1 to 2.5 ethylene oxide carbons per primary alcohol carbon. On the other hand, as will be more fully hereinafter described, there is a substantial color enhancement when part of the ethylene oxide is replaced with, or supplemented by, propylene oxide.

Increase in the proportion of detergent to iodine provides a distinct enhancement of color intensity at low use dilutions. In moving from a 5 to 1 to 10 to 1 detergent to iodine ratio, the color intensity is generally about doubled. This is of special significance in view of the fact that, for compositions with recommended sanitation uses below the 25 p.p.m. iodine level, it is desirable to use progressively higher ratios of detergent to iodine, in order to provide an effective amount of detergent in the more dilute use solutions.

As a means for reliably recording and comparing color in detergent-iodine solutions, it is practical to use an instrument such as a Beckman spectrophotometer. Color is measured in terms of absorbance, a decimal value obtained as

$$\log \frac{I_0}{I}$$

i.e.

$$\log \frac{\text{light in}}{\text{light out}}$$

for a 1 cm. spectrophotometer sample cell.

Iodine has been used recently to measure the critical micelle concentration (cmc) of nonionic detergents. S. Ross and J. P. Olivier, in a paper entitled "A Method for the Determination of Critical Micelle Concentrations of Un-ionized Association Colloids in Aqueous or in Non-aqueous Solutions" (J. Phys. Chem. 63 1671 (1959)) describe how solutions of elemental iodine can be used to determine the cmc in much the same way as with dyes, which are frequently used for cmc determinations. The iodine is superior to dyes in general owing to the small molecular size of iodine compared to dyes; the iodine thereby does not interfere appreciably with the detergent agglomerate. A 25 p.p.m. aqueous solution of elemental iodine was used by Ross, to which were added varying amounts of a stock detergent solution. The light absorption at  $360\text{ m}\mu$  was measured and was plotted as a function of detergent concentration. The inflection point in this graph was taken as the cmc value. The maximum light absorption in Ross' experiments was always found at  $360\text{ m}\mu$ .

There is no relationship between the novel subject matter of this application and any of the subject matter in the above reference for the following reasons. It has been

found that detergent-iodine solutions characteristic of the environmental sanitation art, exhibit absorption peaks considerably closer to the visible region. That is, as shown below, the peak values are at 385-398 m $\mu$  rather than at 360 m $\mu$ . This is an important difference in that any visual utility of such results depends on the magnitude of the portion of the curve which is beyond 400 m $\mu$  in the visible region. The peak value is a good representation of, and is proportional to, the values beyond 400 m $\mu$ . It is customary to read absorption at the peak value, since this gives the highest degree of accuracy.

Ross' results give absolutely no insight into the relationship between color and chemical constitution within the members of a homologous series. One might therefore incorrectly predict from Ross' results that the addition of further ethylene oxide to a water-soluble molecule, which increases the cmc, would result in a detergent which would show less color with iodine, since an equivalent concentration would bring it closer to its inflection point. This is certainly not the general case when detergents having the same starting alcohol are compared. Table A shows that the results for the pairs No. 2 and No. 4 and No. 14 and No. 15 gives the opposite effect. The series No. 11, No. 12, and No. 13 which shows a small decrease because the results are given on a weight percent basis, actually reverse when the detergent concentrations are given on a molecular weight basis.

For the purpose of evaluating detergent-iodine compositions of the present invention, however, it is essential that elemental or available iodine be distinguished from iodide which may be formed in, or added to, the composition. It has been found, for example, that while addition of iodide to a detergent-iodine solution provides some enhancement of color, it is of small magnitude compared to the color change with variations of available iodine concentration. Since iodide alone with detergent produces no color, the color enhancement above mentioned indicates intensifying of color of the detergent-iodine complex in the presence of iodide.

An effective measure of the iodine complexing in the new detergent-iodine compositions is the distribution coefficient (D.C.) determined in a two-phase aqueous-heptane system according to the procedure disclosed in the above mentioned United States Patent No. 3,028,229. Surprisingly, a number of the new compositions in which iodine is complexed with a C<sub>12</sub> to C<sub>18</sub> primary alcohol-ethylene oxide condensate, show substantially higher D.C. values than similar compositions containing the conventional nonyl-phenol-ethylene oxide condensate.

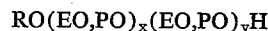
A final standard to be considered in evaluating the new compositions is cloud point. This is the temperature above which detergents and detergent-iodine complexes in aqueous solution change from clear or transparent solutions to cloudy solutions or suspensions. In general, the cloud point of liquid germicidal products or concentrates should be at least 50° C., and preferably above about 55° C. in order that such products will remain clear and transparent under all normal storage conditions.

The unique color enhancing properties as above described for the C<sub>12</sub> to C<sub>18</sub> primary alcohol-ethylene oxide condensates complexed with iodine are also found to be present to a substantial extent in detergent-iodine complexes in which the detergent is a condensate of ethylene oxide with an alkyl phenol in which the alkyl substituent comprises one or more primary aliphatic radicals having a total of 12 to 18 carbon atoms. Typical examples of such detergents are condensates of ethylene oxide with dodecylphenol, dioctylphenol, and dinonylphenol in which the amount of ethylene oxide is at least sufficient to impart water solubility to the detergent. Suitably, the number of moles of ethylene oxide can be in the range of about .8 to 3 times the number of carbon atoms in the alkyl substituent.

Under comparable conditions, these higher alkyl-phenol-ethylene oxide condensates provide iodine complexes

having more than twice the color intensity at 6 p.p.m. available iodine dilutions than complexes formed with the conventional nonylphenol-ethylene oxide condensates.

Another embodiment of the present invention resides in the discovery that still further color enhancement can be achieved with the primary alcohol type detergents if at least part of the condensed ethylene oxide is replaced with, or supplemented by, propylene oxide. Such modified detergents can be represented by the following formula:



wherein R is C<sub>12</sub> to C<sub>18</sub> primary alkyl, the weight percent of EO is within the range of 0 to 45% in one of the blocks, x, y and within the range 60 to 100% in the other of the blocks x, y, and the total number of moles of alkoxide is in the range of 6 to 40 moles, with 1 to 10 moles in the PO rich block, and 5 to 30 moles in the EO rich block.

Generally preferred among the detergents above described are those in which the block x contains 0 to 45% EO, and provides 1 to 4 moles of alkoxide, while the block y contains 60 to 90% EO, and provides 5 to 20 moles of alkoxide.

Preferred detergents of this modified type provide iodine complexes having under comparable conditions, a color intensity at 6 p.p.m. dilution which is more than four times as great as the conventional nonyl-phenol ethylene oxide-iodine complex. Furthermore, the modified detergents can be in liquid form even when the average number of carbon atoms in the radical R is as high as C<sub>16</sub>. Both of these factors are of distinct advantage in the formulation and use of germicidal detergent-iodine compositions.

The following examples show the preparation of typical detergent-iodine compositions suited for varied environmental sanitation uses and employing the color enhancing detergent-iodine complexes of the present invention. It is to be understood however, that these examples are given by way of illustration and not of limitation.

#### Example I

A number of detergent iodine compositions were prepared using various primary alcohol-ethylene oxide condensates as detergents. These compositions are all aqueous solutions containing 10% detergent, 1% available iodine, and 0.35% iodide (I<sup>-</sup>) by weight, the iodine and iodide being supplied as HI-Iodine solution containing 57% available iodine and 20% HI.

In Table A, detergents are identified by the number of carbon atoms in the primary alcohol component, the number of moles of condensed ethylene oxide, the cloud point of a 1% aqueous solution, and the physical state at 25° C. For the resulting detergent-iodine compositions, values are given for distribution coefficient (D.C.) as determined by the formula:

$$\text{D.C.} = \frac{\text{mg. I in aqueous phase}}{\text{mg. I in heptane}} \times \frac{\text{ml. heptane}}{\text{ml. aqueous phase}}$$

In addition, the relative color of diluted solutions having available iodine concentrations of 25 p.p.m., 12.5 p.p.m., and 6 p.p.m., are tabulated, together with the wave length in m $\mu$  of the peak position, or maximum absorbance, for the 25 p.p.m. solution. Relative color or absorbance refers to

$$\log \frac{I_0}{I}$$

for unit path length, where I<sub>0</sub> and I are the "light in" and "light out" respectively. A Beckman Du spectrophotometer with cells of 1.00 cm. path length were used.

TABLE A

| Sample No. | Atoms of Carbon | Mols ETO | Cloud Point, ° C. | Phys. State at 25° C. | Relative Color (Absorbance) |           |             |          | 25 p.p.m. Peak (mμ) |
|------------|-----------------|----------|-------------------|-----------------------|-----------------------------|-----------|-------------|----------|---------------------|
|            |                 |          |                   |                       | D.C.                        | 25 p.p.m. | 12.5 p.p.m. | 6 p.p.m. |                     |
| 1-----     | 11 av. (10-12)  | 5.9      | 27                | Liquid                | ---                         | .245      | .045        | .010     | 360                 |
| 2-----     | 12 av. (10-14)  | 7.0      | 64                | do                    | 67                          | .670      | .145        | .035     | 385                 |
| 3-----     | 12 av. (10-16)  | 7.4      | 64                | do                    | 79                          | .715      | .220        | .050     | 385                 |
| 4-----     | 12 av. (10-14)  | 15       | >100              | Solid                 | 94                          | .720      | .195        | .045     | 390                 |
| 5-----     | 12              | 9.5      | 84                | Liquid                | 83                          | .805      | .235        | .045     | 385                 |
| 6-----     | 14 av. (12-20)  | 8.5      | 65                | do                    | 100                         | .800      | .245        | .065     | 390                 |
| 7-----     | 14 av. (12-18)  | 7.5      | 61                | do                    | 96                          | .735      | .220        | .060     | 385                 |
| 8-----     | 14 av. (12-18)  | 8.1      | 65                | do                    | 102                         | .795      | .240        | .060     | 390                 |
| 9-----     | 14              | 7.6      | 63                | do                    | 86                          | .900      | .310        | .090     | 385                 |
| 10-----    | 14              | 9.2      | 82                | Solid                 | 95                          | .885      | .300        | .085     | 385                 |
| 11-----    | 16              | 7.4      | ---               | do                    | 103                         | .790      | .275        | .090     | 385                 |
| 12-----    | 16              | 10       | 76                | do                    | 127                         | .720      | .245        | .070     | 385                 |
| 13-----    | 16              | 20       | >100              | do                    | 107                         | .705      | .240        | .065     | 385                 |
| 14-----    | 18              | 10       | 68                | do                    | 86                          | .670      | .240        | .080     | 390                 |
| 15-----    | 18              | 20       | >100              | do                    | 76                          | .820      | .300        | .105     | 390                 |
| Control A  | Nonylphenol     | 10.5     | ---               | Liquid                | 75                          | .660      | .160        | .025     | 385                 |
| Control B  | "Pluronic P-65" | ---      | 84                | do                    | 80                          | .150      | .044        | .009     | 360                 |

In Control A sample, the detergent is a nonyl phenol ethylene oxide condensate widely used in detergent-iodine compositions. Control B, another nonionic detergent extensively used in detergent-iodine compositions is a condensate of polyoxypropylene having a molecular weight of 1750 with ethylene oxide in an amount to provide 50% by weight in said condensate. All samples, with the exception of 1 and 2 show much better color at all dilutions, and particularly at the 6 p.p.m. dilution where any increase of color is of very real significance.

Sample I is included for comparison purposes to show the poor color obtained when the starting alcohol is below the C<sub>12</sub>-C<sub>18</sub> range. The color is most deficient at the levels of 6 and 12.5 p.p.m. available iodine.

Sample 2, approximately equal to the Control A, represents a combination of minimum length carbon chain in the alcohol moiety and minimal ethylene oxide.

The preferred samples in Table A are considered to be 8, 9 and 15. The detergents in both 8 and 9 are liquids, which as previously indicated, are preferable to solids, and

TABLE B

| Sample  | Absorbance at mμ |      |      |      |      |      |      |      |      |
|---------|------------------|------|------|------|------|------|------|------|------|
|         | 350              | 360  | 370  | 380  | 385  | 390  | 400  | 425  | 450  |
| 8-----  | .625             | .635 | .740 | .780 | .790 | .795 | .745 | .490 | .290 |
| 9-----  | .690             | .760 | .825 | .880 | .900 | .895 | .830 | .550 | .325 |
| 15----- | .640             | .695 | .760 | .805 | .820 | .820 | .790 | .545 | .330 |

## Example II

In order to demonstrate the effect of variation in the proportion of detergent, compositions similar to the preferred samples 8, 9 and 15 of Example I (and here identified as 8a, 9a and 15a) were prepared having 50%, 100%, 150% and 200% of the amount of detergent used in Example I, and these compositions at varying dilutions were tested for absorbance with the followings results:

| P.p.m. Det. | Relative Color as a Function of Detergent Concentration |     |      |      |                                                         |     |      |      |                                                    |     |      |      |
|-------------|---------------------------------------------------------|-----|------|------|---------------------------------------------------------|-----|------|------|----------------------------------------------------|-----|------|------|
|             | 25 p.p.m. I <sub>2</sub><br>9 p.p.m. I <sup>-</sup>     |     |      |      | 12.5 p.p.m. I <sub>2</sub><br>4.5 p.p.m. I <sup>-</sup> |     |      |      | 6 p.p.m. I <sub>2</sub><br>2 p.p.m. I <sup>-</sup> |     |      |      |
|             | 125                                                     | 250 | 375  | 500  | 62                                                      | 125 | 187  | 250  | 31                                                 | 62  | 93   | 125  |
|             | 8a                                                      | 9a  | 15a  |      | 8a                                                      | 9a  | 15a  |      | 8a                                                 | 9a  | 15a  |      |
| 8a-----     | .40                                                     | .80 | .91  | 1.07 | .11                                                     | .24 | .285 | .360 | .02                                                | .06 | .065 | .10  |
| 9a-----     | .50                                                     | .80 | 1.03 | 1.17 | .15                                                     | .24 | .355 | .425 | .03                                                | .06 | .10  | .125 |
| 15a-----    | .48                                                     | .82 | .98  | 1.12 | .15                                                     | .30 | .360 | .450 | .04                                                | .10 | .10  | .145 |

the detergent of 8 is somewhat more readily available than that of 9. As for sample 15, the disadvantage of the solid form of the detergent is offset by the unusually high color value at the 6 p.p.m. dilution.

With respect to the three preferred samples, there is shown in the following tabulation, the variation of absorbance at different wave lengths (mμ) for the 25 p.p.m. dilution.

The foregoing comparisons indicate that increasing the proportion of detergent causes an increase in the color intensity at all dilutions, with the effect being greatest at the 6 p.p.m. iodine concentration, where enhancement of color is of greatest importance. The data further indicates that the color improvement increases most rapidly when the proportion of detergent to available iodine increases from 5:1 to 10:1.

## Example III

In order to demonstrate the effect of variation in the proportion of iodide, compositions similar to the preferred samples 8 and 9 of Example I (and here identified as 8b and 9b) were prepared having iodide proportions equal to and approximately four times as great as in Example I, and these compositions at varying dilutions were tested for absorbance with the following results:

|         | Relative Color as a Function of Iodine Concentration |                          |                                                    |                          |                                                |                         |
|---------|------------------------------------------------------|--------------------------|----------------------------------------------------|--------------------------|------------------------------------------------|-------------------------|
|         | 250 p.p.m. Detergent<br>25 p.p.m. I <sub>2</sub>     |                          | 125 p.p.m. Detergent<br>12.5 p.p.m. I <sub>2</sub> |                          | 63 p.p.m. Detergent<br>6 p.p.m. I <sub>2</sub> |                         |
|         | 9 p.p.m. I <sup>-</sup>                              | 34 p.p.m. I <sup>-</sup> | 4.5 p.p.m. I <sup>-</sup>                          | 17 p.p.m. I <sup>-</sup> | 2 p.p.m. I <sup>-</sup>                        | 8 p.p.m. I <sup>-</sup> |
| 8b..... | .80 (390 mμ)                                         | .92 (380 mμ)             | .240                                               | .330                     | .060                                           | .085                    |
| 9b..... | .90 (385 mμ)                                         | 1.06 (380 mμ)            | .310                                               | .395                     | .090                                           | .125                    |

The foregoing comparisons indicate that small variations in iodide content do not have too great an effect on color. The color enhancement which characterizes the primary alcohol-ethylene oxide detergents as iodine complexing agents can be realized when formulating by both the standard hot mix method and by the cold process using aqueous iodine-iodide solution.

## Example IV

A commercial high acid detergent iodine composition used for dairy and similar cleaning operations, and having a guaranteed available iodine content of 1.75%, contains by weight 19% detergent (a mixture of 15.7 parts nonyl phenol ethylene oxide condensate containing 10.5 moles of ethylene oxide per mole of nonyl phenol and 3.3 parts of polyoxypropylene condensed with ethylene oxide providing a molecular weight of 1750 in the polyoxypropylene component and 20% of condensed ethylene oxide), 3.3% of HI-iodine (supplied as an aqueous solution containing 57% available iodine and 20% HI) 21.25% of H<sub>3</sub>PO<sub>4</sub> (commercial 75% acid) and water to 100%.

With this product as a control, similar products were prepared substituting as detergent 19% of certain of the primary alcohol ethylene oxide condensates of Example I. For ease of cross-reference, these detergents are here identified by the same sample number followed by the subscript "c."

These samples and the control are compared in terms of cloud point and distribution coefficient (D.C.) of the product and the absorbance of 1 to 640 (12.5 p.p.m. I<sub>2</sub>) use dilutions thereof, with the results shown in the following table:

| Sample       | Product Characteristics |      | 1 to 640<br>(12.5 p.p.m. I <sub>2</sub> )<br>Dilution<br>Absorbance |
|--------------|-------------------------|------|---------------------------------------------------------------------|
|              | Cloud Point,<br>° C.    | D.C. |                                                                     |
| Control..... | 55                      | 200  | .255                                                                |
| 2c.....      | 56                      | 200  | .355                                                                |
| 3c.....      | 64                      | 230  | .410                                                                |
| 8c.....      | 66                      | 240  | .405                                                                |
| 9c.....      | 64                      | —    | .450                                                                |
| 13c.....     | >90                     | 380  | .415                                                                |
| 15c.....     | >90                     | —    | .445                                                                |

The tested samples show generally better cloud points and distribution coefficients than the control, and of particular significance is the markedly higher absorbance at the practical 12.5 p.p.m. I<sub>2</sub> use dilution.

## Example V

A germicidal detergent-iodine concentrate is prepared by mixing together at room temperature 360 grams of an HI-I<sub>2</sub> solution as described in Example I and 640

grams of a C<sub>14</sub> primary alcohol-ethylene oxide condensate containing 8.1 moles of ethylene oxide (detergent No. 8 in Example I) forming a clear, dark mahogany colored liquid having a specific gravity at 60° F. of 1.276 and a viscosity at 20° C. of 280 c.p.s. Immediately after preparation, the available iodine was 20.4%, and after accelerated ageing by storing for two weeks at 125° F., the available iodine was found to be 20.2% (indicating very good stability).

This concentrate is suitable for sale and distribution to formulators who will add water, acid, additional detergent, or combinations of these in preparing consumer products.

Examples I to V show the advantages of primary alcohol ethylene oxide condensates as detergent components of detergent-iodine compositoins. The following three examples are included to demonstrate the unsatisfactory nature of secondary alcohol-ethylene oxide condensates.

## Example VI

Two of the detergent-iodine compositions of Example IV, samples 8c and 9c are compared with similar detergent-iodine compositions containing as detergent component Secondary A—a secondary alcohol containing 11 to 15 (average 13) carbon atoms condensed with 9 moles of ethylene oxide—and Secondary B—a secondary alcohol containing 11 to 15 (average 13) carbon atoms condensed with 13 moles of ethylene oxide.

The samples were tested for initial available iodine content, then subjected to industry standardized accelerated storage conditions by maintaining at 125° F. for two weeks and again tested for available iodine, with the following results:

| Sample           | Initial I <sub>2</sub> , percent | Stored two weeks<br>at 125° F.<br>I <sub>2</sub> , percent |
|------------------|----------------------------------|------------------------------------------------------------|
| 8c.....          | 1.93                             | 1.82                                                       |
| 9c.....          | 1.95                             | 1.89                                                       |
| Secondary A..... | 1.93                             | 1.67                                                       |
| Secondary B..... | 1.92                             | 1.66                                                       |

Since as noted in Example IV this type product should have a guaranteed iodine content of 1.75%, it is apparent that the secondary A and B samples are unsatisfactory, whereas the 8c and 9c samples show very little iodine loss in the accelerated ageing test. The two weeks at 125° F. is generally comparable to a full year under normal storage conditions.

## Example VII

A typical detergent-iodine composition without phosphoric acid, intended for general environmental sanitation purposes, and having a guaranteed available iodine content of 1.6% contains 15% detergent, 3.3% HI-iodine (supplied as an aqueous solution containing 57% available iodine and 20% HI), 2% of isopropyl alcohol, and water to 100%.

This type composition was made up using the two preferred detergents from Example I, here identified as 8d and 9d, and the two detergents derived from secondary alcohols, Secondary A and Secondary B as described in Example V, and were tested for available iodine before

and after the standard two weeks, storage at 125° F., with the following results:

| Sample      | Initial I <sub>2</sub> , percent | Stored two weeks at 125° F. I <sub>2</sub> , percent |
|-------------|----------------------------------|------------------------------------------------------|
| 8d          | 1.91                             | 1.71                                                 |
| 9d          | 1.91                             | 1.77                                                 |
| Secondary A | 1.93                             | 1.56                                                 |
| Secondary B | 1.92                             | 1.56                                                 |

Here again the compositions using ethoxylated secondary alcohols as the detergent component fall below the guaranteed iodine content in the standard accelerated ageing test. Furthermore, comparing Examples V and VI serves to indicate that the presence of the phosphoric acid was not a factor, but that the poor results with the ethoxylated secondary alcohols must be due to a chemical instability, i.e. a reactivity between the secondary alcohol moiety and the iodine. This is further confirmed by the following example:

#### Example VIII

Following the conventional formulating procedure of

this connection, that the appearance of color in the detergent per se is particularly objectionable as it would mask and destroy the important iodine color end point, thus further demonstrating the instability of secondary alcohol-ethylene oxide condensates as iodine carriers.

Embodiments of the invention wherein detergent-iodine complexes having enhanced color at low use dilutions are obtained with detergents other than the C<sub>12</sub> to C<sub>18</sub> primary alcohol ethylene oxide condensates are illustrated in the following examples:

#### Example IX

Following the procedure of Example I an aqueous detergent-iodine solution containing by weight 10% detergent, 1% available iodine and 0.35% iodide (I<sup>-</sup>) using as detergent dodecylphenol condensed with 12 moles of ethylene oxide. This detergent is a liquid at 25° C. and in 1% aqueous solution has a cloud point of 60°. The detergent-iodine solution has a distribution coefficient of 64 and when tested for relative color or absorbance as in Example I, gave results shown in the following tabulation, and compared with the values for Control A from Example I:

| Detergent                  | Relative Color (absorbance) |             |          | 25 p.p.m. peak (m <sub>μ</sub> ) |
|----------------------------|-----------------------------|-------------|----------|----------------------------------|
|                            | 25 p.p.m.                   | 12.5 p.p.m. | 6 p.p.m. |                                  |
| Dodecylphenol 12 moles EtO | .710                        | .215        | .055     | 385                              |
| Nonylphenol 10.5 moles EtO | .660                        | .160        | .025     | 385                              |

cooking detergent and elemental iodine for about 4 hours at 55 to 60° C., comparative formulations were prepared using 72 parts of detergent and 28 parts of elemental iodine, the cooking being effected in a three necked flask equipped with Teflon stirrer, thermometer and pressure equalization port. Following the heating period, the batch was cooled, analyzed for available iodine, and the residual color after neutralizing the iodine with thiosulfate was noted.

The sample marked "Primary" employed the preferred ethoxylated primary alcohol (sample 8 of Example I) and the sample marked "Secondary" used the ethoxylated secondary alcohol described as Secondary A in Example V.

The comparative results are as follows:

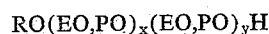
| Sample    | Percent Available I <sub>2</sub> |       | Average Temp., °C. | Final Detergent Color |
|-----------|----------------------------------|-------|--------------------|-----------------------|
|           | Theory                           | Found |                    |                       |
| Primary   | 28.0                             | 25.0  | 57                 | Colorless.            |
| Secondary | 28.0                             | 22.0  | 57                 | Very dark "Caramel."  |

Both the high iodine loss and the charred color of the detergent confirm the suspected reactivity of iodine with the secondary alcohol type detergent. It will be noted in

This enhancement of color in dilute solutions is characteristic of detergent-iodine complexes containing as detergent component alkylphenol-ethylene oxide condensates in which primary alkyl substituents provide 12 to 18 carbon atoms, with the color enhancement generally increasing as the number of carbon atoms is increased.

#### Example X

Following the procedure of Example I and IX aqueous detergent-iodine solutions were prepared containing as detergent components condensates of primary alcohols in the C<sub>12</sub> to C<sub>18</sub> range with mixtures of ethylene oxide and propylene oxide providing the compositions tabulated below, having reference to the formula:



| Detergent | Carbon in R | Wt. percent EO in— |     | Moles EO+PO in— |      |
|-----------|-------------|--------------------|-----|-----------------|------|
|           |             | "x"                | "y" | "x"             | "y"  |
| a         | 14          | 25                 | 75  | 4.0             | 13.7 |
| b         | 14          | 75                 | 25  | 13.7            | 4.0  |
| c         | 15          | 25                 | 75  | 4.3             | 14.6 |
| d         | 12          | 25                 | 75  | 3.4             | 11.7 |
| e         | 14          | 15                 | 85  | 3.9             | 14.0 |
| f         | 14          | 30                 | 70  | 4.0             | 13.5 |
| g         | 14          | 30                 | 70  | 2.4             | 10.8 |
| h         | 13.5        | 33                 | 67  | 2.7             | 12.4 |

The detergents and the aqueous solutions of their iodine complexes were tested as in Example I, and the results are tabulated below together with the values for preferred samples 8, 9 and 15 from Example I:

| Sample    | Detergent             |                              | Aqueous Complex             |           |             |          | 25 p.p.m.<br>peak<br>(mμ) |
|-----------|-----------------------|------------------------------|-----------------------------|-----------|-------------|----------|---------------------------|
|           | Cloud<br>Pt.,<br>° C. | Physical<br>State,<br>25° C. | Relative Color (absorbance) |           |             |          |                           |
|           |                       |                              | D.C.                        | 25 p.p.m. | 12.5 p.p.m. | 6 p.p.m. |                           |
| a.....    | 64                    | Liquid                       | 75                          | .880      | .295        | .080     | 390                       |
| b.....    | 64                    | do.                          | 70                          | .870      | .275        | .070     | 390                       |
| c.....    | 65                    | do.                          | 92                          | 1.045     | .355        | .110     | 390                       |
| d.....    | 64                    | do.                          | 95                          | .840      | .245        | .060     | 385                       |
| e.....    | 73                    | do.                          | 70                          | .940      | .315        | .085     | 390                       |
| f.....    | 58                    | do.                          | 75                          | .890      | .295        | .085     | 390                       |
| g.....    | 55                    | do.                          | 70                          | .905      | .290        | .075     | 390                       |
| h.....    | 54                    | do.                          | 65                          | .950      | .315        | .085     | 390                       |
| i-8.....  | 65                    | do.                          | 102                         | .795      | .240        | .060     | 390                       |
| i-9.....  | 63                    | do.                          | 86                          | .900      | .310        | .090     | 385                       |
| i-15..... | >100                  | Solid                        | 76                          | .820      | .300        | .105     | 390                       |

hol moiety with an average carbon content within the range of C<sub>12</sub> to C<sub>18</sub>, and

$$\frac{n}{2} - 1$$

It is significant to note that Sample c provides distinctly better color at the three dilutions than the comparative samples from Table I and that the color value at each dilution is at least 10% better than the values for sample I-9, which is the best performing liquid detergent in Example I. The color values for sample "c" in which R represents C<sub>12</sub> are substantially higher than the comparable color values for samples 2, 3, 4 and 5 in Table A of Example I. There is therefore a clear indication from the color values for samples "a" to "h" above that the basic increase in color when increasing the alkyl carbon content above C<sub>12</sub> is amplified by the substitution of the mixed EO,PO for the ethylene oxide of Example I as the alkoxide component of the detergent.

In summary, it is to be noted that while three apparently quite different type detergents have been described in the foregoing examples, they share the common and highly practical characteristic of providing enhancement in iodine color at all conventional use dilutions and at dilutions heretofore considered impractical due to the faintness or absence of iodine color. Expressed in another way, the new detergent-iodine complexes coming within the present invention are those characterized as providing enhanced iodine color as evidenced by an absorbance,

$$\log \frac{I_0}{I}$$

1 cm., of greater than .035, and preferably at least .045 when measured at the 6 p.p.m. available iodine level with a 10:1 ratio of detergent to iodine. Complexes of the three types described which measure up to this characteristic, and have a detergent to available iodine ratio of at least 3:1, and detergent-iodine compositions containing such complexes are considered as falling within the present invention, no matter whether such compositions are in the form of commercial concentrates, consumer products intended for dilution, or end use products adapted for use without dilution.

Various changes and modifications in the detergent-iodine compositions herein disclosed will occur to those skilled in the art, and to the extent that such changes and modifications are embraced by the appended claims, they constitute part of the present invention.

We claim:

1. A detergent-iodine composition providing enhanced iodine color in high use dilution, said composition consisting essentially of a detergent-iodine complex providing a germicidally effective amount of iodine, the detergent component of said complex being a water soluble primary alcohol-ethylene oxide condensate having an alco-

25 to 2n-1 mols of ethylene oxide, where n is the average number of carbon atoms in said alcohol moiety, the ratio of detergent to available iodine in said complex being at least 5:1.

2. A detergent-iodine composition as defined in claim 1 wherein said alcohol moiety has an average number of carbon atoms within the C<sub>14</sub> to C<sub>18</sub> range.

3. A detergent-iodine composition as defined in claim 1 wherein said detergent is a liquid condensate of a C<sub>12</sub> to C<sub>14</sub> primary alcohol with at least 7.5 moles of ethylene oxide.

4. A detergent-iodine composition as defined in claim 1 wherein said detergent is a liquid condensate of a primary alcohol having an average carbon content of C<sub>14</sub> with about 7.6 moles of ethylene oxide.

5. A detergent-iodine composition as defined in claim 1 wherein said detergent is a liquid condensate of a C<sub>14</sub> primary alcohol with about 8.1 moles of ethylene oxide.

6. A detergent-iodine composition as defined in claim 1 wherein said detergent is a solid condensate of a primary alcohol having an average carbon content within the C<sub>16</sub> to C<sub>18</sub> range with about 10 to 20 moles of ethylene oxide.

7. A detergent-iodine composition as defined in claim 1 wherein said detergent is a solid condensate of a C<sub>18</sub> primary alcohol with about 20 moles of ethylene oxide.

8. A detergent-iodine composition as defined in claim 1 wherein the detergent:iodine ratio is within the range of 5:1 to 20:1.

9. A detergent-iodine composition providing enhanced iodine color in high use dilution, said composition consisting essentially of a detergent-iodine complex providing a germicidally effective amount of iodine, the detergent component of said complex being a water soluble alkyl-phenol-ethylene oxide condensate in which the alkyl substituent comprises one or more primary aliphatic radicals having a total of 12 to 18 carbon atoms, and the number of mols of ethylene oxide is within the range of 0.8 to 3.0 times the number of carbon atoms in said alkyl substituent, the ratio of detergent to available iodine in said complex being at least 5:1.

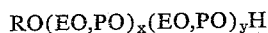
10. A detergent-iodine composition as defined in claim 9 wherein said detergent is a condensate of dodecylphenol with 12 moles of ethylene oxide.

11. A detergent-iodine composition as defined in claim 9 wherein the detergent:iodine ratio is within the range of 5:1 to 20:1.

12. A detergent-iodine composition providing enhanced iodine color in high use dilution, said composition consisting essentially of a detergent-iodine complex providing

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a germicidally effective amount of iodine, the detergent component of said complex being a water soluble primary alcohol-alkylene oxide condensate represented by the formula



wherein R is C<sub>12</sub> to C<sub>18</sub> primary alkyl, EO and PO represent ethylene oxide and propylene oxide respectively, the weight percent of EO is within the range of 0 to 45% in one of the blocks x, y and within the range of 60 to 100% in the other of the blocks x, y, and the total number of moles of combined EO and PO is in the range of 6 to 40 moles, with 1 to 10 moles in the PO rich block, and 5 to 30 moles in the EO rich block, the ratio of detergent to available iodine in said complex being at least 5:1.

13. A detergent-iodine composition as defined in claim 12 wherein the block x contains 0 to 45% EO and provides 1 to 4 moles of alkoxide, and the block y contains 60 to 90% EO and provides 5 to 20 moles of alkoxide.

14. A detergent-iodine composition as defined in claim 12 wherein the block x contains 25% EO and provides

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4.3 moles of alkoxide, the block y contains 75% EO and provides 14.6 moles of alkoxide, and R is C<sub>15</sub> alkyl.

15. A detergent-iodine composition as defined in claim 12 wherein the detergent:iodine ratio is within the range of 5:1 to 20:1.

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