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3,513,098

GERMICIDAL NONIONIC DETERGENT-IODINE COMPOSITIONS

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3 Claims

ABSTRACT OF THE DISCLOSURE

Aqueous nonionic detergent-iodine compositions providing enhanced iodine color in high use dilution, wherein the detergent is a water soluble secondary alcohol-ethylene oxide condensate having an alcohol moiety with an average carbon content within the C₁₄ to C₁₅ range and 8 to 13 moles of ethylene oxide, the ratio of detergent to available iodine being at least 5:1, and said aqueous composition containing a source of iodide (I⁻) in excess of 0.25 part per part of available iodine. In preferred compositions the detergent is a liquid condensate of a C₁₄-C₁₅ secondary alcohol and about 8 to 10 moles of ethylene oxide.

BACKGROUND OF THE INVENTION

The concept of providing enhanced iodine color in high use dilutions of nonionic detergent-iodine compositions by appropriate selection and balancing of the carbon content of the hydrophobic portion and the alkylene oxide content of the hydrophilic portion of the detergent used in such compositions was first disclosed in applicants' pending application Ser. No. 498,130, now Pat. No. 3,355,368. Among the several type detergents therein disclosed as capable of providing enhanced iodine color at high use dilution were water soluble primary alcohol-ethylene oxide condensates having an alcohol moiety with an average carbon content within the range of C₁₂ to C₁₈, and

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

moles of ethylene oxide, where n is the average number of carbon atoms in said alcohol moiety.

The use of secondary alcohol-ethylene oxide condensates is expressly excluded from the subject matter to be covered by said application on the basis of the instability of secondary alcohol-detergent-iodine compositions and the poor iodine color at high dilution with the secondary alcohol-ethylene oxide condensates then available. Such instability is evidenced by iodine loss in storage as shown in Examples VI and VII and more particularly by the charring which results in the normal hot formulating process of making detergent iodine complexes as shown in Example VIII. These examples are based on the then available secondary alcohol ethylene oxide condensates containing an alcohol moiety with an average of 13 carbon atoms and 9 to 13 moles of ethylene oxide. Furthermore these secondary alcohol ethylene oxide condensates, even when formulated with ethylene oxide by the cold mixing process with iodine supplied as an aqueous iodide-iodine described in U.S.

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Pat. 3,028,299, and as employed in Example VI and VII of said application (so that no extraneous color was produced due to charring), showed iodine color at high dilution which was no better than that with conventional detergents such as nonyl phenol condensed with about 10 moles of ethylene oxide.

THE INVENTION

It has now been discovered that when iodine is complexed by the cold mixing process with a secondary alcohol-ethylene oxide containing an average of 14 to 15 carbon atoms in the alcohol moiety and about 8 to 13 moles of ethylene oxide the resulting detergent-iodine composition shows a marked enhancement of iodine color at high use dilution. This could not have been determined at the time of filing said pending application since the C₁₄-C₁₅ secondary alcohol condensates were not available at that time. In fact, it is only in recent months, with the growing interest in a broadened range of biodegradable detergents, that the C₁₄-C₁₅ secondary alcohol ethylene oxide condensates have become available in experimental amounts; and they are a long way from becoming available in commercial quantities.

It is indeed surprising that such a small change in the alcohol moiety, i.e., from an average of 13 carbon atoms to an average of 14-15 carbon atoms in the alcohol moiety, should have such a marked effect on the iodine color at high use dilutions of the detergent-iodine complexes. It is speculated that moving to a still higher carbon content might produce a further color enhancement, but such secondary alcohol-ethylene oxide condensates are not even available in experimental amounts.

The C₁₄-C₁₅ secondary alcohol ethylene oxide condensates share to a substantial extent the instability above described as characterizing the C₁₃ compounds, but the instability as it pertains to color can be offset by formulating detergent-iodine complexes in aqueous solution by the cold mixing process. Thus compositions of the present invention will necessarily contain the excess of iodide ion I⁻ which is introduced in the cold mixing process. As disclosed in U.S. Pat. 3,028,299 the iodide ion (I⁻), supplied by HI or by a water soluble iodide salt, should be present in the resulting aqueous solution of the complex in an amount to provide in excess of 0.25 part of iodide (I⁻) per part by weight of iodine.

As shown in the examples hereinafter appearing the loss of available iodine on storage of the new compositions is greater than with compositions formulated with primary alcohol-ethylene oxide condensates, but this iodine loss is less pronounced with the C₁₄-C₁₅ secondary alcohol moiety than with the C₁₃ secondary alcohol moiety in the detergent component. Furthermore, the accelerated aging test which involves storing for two weeks at 125° F. is comparable to more than a full year under normal storage conditions. Thus for compositions which do not require extended storage and for uses and applications where the detergent characteristics of the C₁₄ to C₁₅ secondary alcohol-ethylene oxide condensate are of special advantage, the fact that there may be some iodine loss on storage becomes of secondary consideration. From a practical standpoint it can be offset by providing an appropriate overage in the amount of available iodine, to assure the maintenance of the label designated amount of available iodine in a commercial product during the anticipated storage period.

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Detergent-iodine compositions embraced by the present invention include compositions containing as little as 0.1% and as much as 25% available iodine with the proportion of detergent to iodine being greater than 5:1 and preferably in the range of 5:1 to 20:1. Commercial products intended for dilution by the consumer in preparing use dilutions will generally contain about 1-15% available iodine. Other type commercial products intended for use without dilution may contain about 0.1-1.0% available iodine. Compositions containing 15-25% available iodine are in the nature of commercial concentrates intended for dilution and further compounding, as, for example, by addition of more detergent, in the formulation of consumer products. In non-acidified products for general en-

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of 385 m μ , which is the peak absorbance wave length for the 25 p.p.m. dilutions.

In the following tabulation the detergents are identified by the number of carbon atoms in the secondary alcohol moiety and the number of moles of condensed ethylene oxide, and the decimal values of absorbance

$$\left(\log \frac{I_0}{I}\right)$$

at the several dilutions are presented. Also included in the tabulation are absorbance values for a similarly formulated control sample in which the detergent is a nonyl phenol-ethylene oxide condensate containing an average of 10.5 moles of ethylene oxide per mole of nonyl phenol.

Detergent Data							
Sample No.	Carbon Atoms in hydrophobe		Moles EO	Physical State, 25° C.	Relative Color at indicated p.p.m.		
	Range	Av.			25	12.5	6
1-----	11-15	13	9	Liquid-----	.600	.150	.030
2-----	11-15	13	13	do-----	.600	.110	.020
3-----	14-15	14.5	8	do-----	.780	.245	.055
4-----	14-15	14.5	10	do-----	.790	.245	.060
5-----	14-15	14.5	13	Paste-----	.765	.215	.045
6-----	14-15	14.5	15	Wax-----	.685	.173	.032
7-----	14-15	14.5	20	Wax-----	.560	.122	.017
8-----	14-15	14.5	30	Wax-----	.330	.051	.010
9-----	Control			Liquid-----	.660	.160	.025

vironmental sanitation purposes the portion of the composition not accounted for by the detergent, iodine, and iodide 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 and compatible acids, such as phosphoric acid, hydroxyacetic acid, and mixtures thereof.

The enhancement of iodine color realized in high use dilutions of the new compositions is of real practical significance since it is recognized that iodine is germicidally active in concentrations as low as fractions of a p.p.m. With the new compositions, for example, there is readily visible iodine color at use dilutions containing 6 p.p.m. of available iodine. Furthermore, increase in the proportion of detergent to iodine provides a distinct enhancement of color at this order of dilution. Thus the normal tendency to increase the proportion of detergent to iodine in order to provide adequate detergency at high use dilutions serves to accentuate and extend the iodine color enhancement achieved with the new compositions.

The following examples show typical detergent-iodine compositions in accordance with the present invention; and in these examples iodine color in use solutions is determined by means of a Beckman spectrophotometer, and 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. 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 secondary alcohol-ethylene oxide condensates as detergents. These compositions are all aqueous solutions containing 10% detergent, 1% available iodine, and 0.35% iodide (I⁻) by weight, the iodine and iodide being supplied as HI-iodine solution containing 57% available iodine and 20% HI.

Use dilutions of these compositions were prepared containing 25, 12.5 and 6 p.p.m. of available iodine, and relative color or absorbance was determined at a wave length

It will be noted that for samples 1 and 2, for which the average carbon content of the hydrophobe is 13, the iodine color is of the same order as that of the control, whereas with samples 3, 4 and 5 in which the average number of carbon atoms in the hydrophobe is 14.5, and the ethylene oxide content is in the range of 8 to 13 moles, the iodine color at the 6 p.p.m. dilution is substantially more intense. In fact, with the preferred, liquid detergents (samples 3 and 4) the color intensity is approximately twice that of samples 1 and 2 and the control. It is particularly significant to note the rapid drop-off of iodine color in samples 6, 7 and 8 as the ethylene oxide content is increased to 15, 20 and 30 moles. This is in distinct contrast to experience with primary alcohol-ethylene oxide condensates where the color drop-off with increased ethylene oxide is very gradual.

Example II

Germicidal detergent-iodine concentrates are prepared by mixing together at room temperature 360 grams of an HI-I₂ solution as described in Example I and 640 grams of the various secondary alcohol-ethylene oxide detergents indicated in the following table forming clear, dark mahogany colored liquid concentrates of a type suitable for sale and distribution to formulators who will add water, acid, additional detergent, or combinations of these in preparing consumer products.

These concentrates were tested for available iodine content promptly after preparation and after storage for two weeks at 125° F. with the results tabulated below. The control sample is a similar concentrate employing as detergent a C₁₄ primary alcohol ethylene oxide condensate containing 8.1 mols of ethylene oxide.

Detergent Data						
Sample No.	Carbon Atoms in hydrophobe		Moles EO	Percent available I ₂		
	Range	Av.		Initial	2 weeks at 125° F	
1-----	11-15	13	13	20.45	19.70	
2-----	14-15	14.5	8	20.45	19.80	
3-----	14-15	14.5	10	20.45	19.80	
4-----	14-15	14.5	13	20.50	20.20	
5-----	Control			20.40	20.20	

Example III

A number of detergent-iodine compositions of the high acid type suitable for dairy cleaning operations (and similar cleaning operations characterized by high concentrations of organic soil), and intended to have a guar-

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anteed available iodine content of 1.75% by weight, were prepared containing by weight:

	Percent
Detergent	19
HI-iodine ¹	3.3
Phosphoric acid (commercial 75% acid)	21.5
Water to 100%.	

¹ Supplied as an aqueous solution containing 57% available iodine and 20% HI.

In five such compositions the detergents were those identified in samples 1 to 5 of Example I, with samples 3, 4 and 5 being the secondary alcohol-ethylene oxide condensates providing enhanced iodine color. In addition, two of the compositions for comparative or control purposes contain primary alcohol-ethylene oxide condensates as the detergent component as follows:

Control A—a liquid condensate of a C₁₂-C₁₈ (average C₁₄) primary alcohol with 8.1 moles of ethylene oxide.
Control B—a liquid condensate of a C₁₄ primary alcohol with 7.6 moles of ethylene oxide.

The seven compositions were tested for available iodine content promptly after preparation and again after two weeks storage at 125° F. with the results indicated in the following tabulation:

Detergent	Percent available I ₂	
	Initial	2 weeks at 125° F.
I-1.....	1.93	1.67
I-2.....	1.92	1.66
I-3.....	1.88	1.52
I-4.....	1.87	1.67
I-5.....	1.87	1.71
Control A.....	1.93	1.82
Control B.....	1.95	1.89

It is apparent that all of the secondary alcohol-ethylene oxide condensates show greater iodine loss than the controls. It is significant, however, to note that with detergents I-3, 4 and 5 there is less of a differential than with detergents I-1 and 2 between the initial percent available iodine and the value after two weeks at 125° F., and the initial percent available iodine is lower. In other words, with these detergents there is somewhat greater iodine loss, due to reaction with the alcohol moiety, at the time of preparation, but less iodine loss during the accelerated aging period.

Example IV

A number of detergent-iodine compositions of the general purpose cleaning and sanitizing type, and intended to have a guaranteed available iodine content of 1.6%, were prepared containing by weight:

	Percent
Detergent	15
HI-iodine ¹	3.3
Isopropyl alcohol	2
Water to 100%.	

¹ Supplied as an aqueous solution containing 57% available iodine and 20% HI.

A total of seven such compositions were prepared using different detergents as described in Example III, and each of these was tested for available iodine content promptly after preparation and again after storage for two weeks at 125° F., with the results as tabulated below:

Detergent	Percent available iodine	
	Initial	2 weeks at 125° F.
I-1.....	1.93	1.56
I-2.....	1.92	1.56
I-3.....	1.84	1.70
I-4.....	1.83	1.66
I-5.....	1.85	1.65
Control A.....	1.91	1.71
Control B.....	1.91	1.71

It is significant to note that compositions containing detergents I-3 to I-5 pass this test, i.e. they have an avail-

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able iodine content after forced aging which is greater than 1.6%, whereas those containing detergents I-1 and I-2 do not pass.

On the basis of the foregoing examples the preferred detergent according to the present invention is a condensate of a C₁₄-C₁₅ (average C_{14.5}) secondary alcohol with 10 moles of ethylene oxide, but a substantial enhancement of iodine color is realized as long as the ethylene oxide content of the detergent is within the range of about 8 to 13 moles.

It has earlier been pointed out that detergent-iodine compositions employing a secondary alcohol-ethylene oxide condensate as the detergent component must be formulated by a cold process, such as the process of U.S. Pat. 3,028,299 wherein iodine is supplied as an aqueous iodide-iodine solution, since the conventional process of dissolving elemental iodine in detergent at elevated temperatures causes charring which masks the desired iodine color. This is clearly demonstrated in the following example.

Example V

A detergent-iodine composition was prepared as in Example II by mixing together at room temperature 640 grams of a C₁₄-C₁₅ (average C_{14.5}) secondary alcohol-ethylene oxide condensate containing 10 moles of ethylene oxide and 360 grams of an HI-iodine solution containing 57% available iodine and 20% HI. This provides approximately 205 grams of available iodine.

A second composition was prepared using 720 grams of the same detergent and dissolving therein 280 grams of elemental iodine by stirring the mixture for about 4 hours at a temperature of approximately 57° C.

The two compositions were analyzed for available iodine immediately after preparation. In quantities of both compositions the iodine was then neutralized with thiosulfate and the residual color of the iodine free solutions noted. The results of these tests are as follows.

Formulating Procedure	Percent available I ₂		Drop in Percent I ₂	Final Detergent Color
	Theory	Found		
Cold process.....	20.5	20.45	0.05	Colorless.
Hot process.....	28.0	22.2	5.80	Very dark "caramel."

Both the high iodine loss and the charred color of the detergent when using the "hot process" formulating procedure indicate that this procedure cannot be used to prepare the detergent-iodine compositions of the present invention. Viewed in another light, the foregoing example demonstrates that the excess iodide, introduced in the "cold process" formulating procedure, is an essential component of the new detergent-iodine compositions.

Various changes and modifications in the detergent-iodine compositions herein disclosed may occur to those skilled in the art, and to the extent that such changes and modifications are embraced by the appended claims it is to be understood that 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 an aqueous solution of a detergent-iodine complex providing a germicidally effective amount of iodine, the detergent component of said complex being a water soluble secondary alcohol-ethylene oxide condensate having an alcohol moiety with an average carbon content within the range of C₁₄ to C₁₅, and 8 to 13 moles of ethylene oxide, the ratio of detergent to available iodine in said complex being at least 5:1, and said aqueous solution containing a source of iodide (I⁻) in excess of about 0.25 part per part of iodine.

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

3. A detergent-iodine composition as defined in claim 1 wherein said detergent is a liquid condensate of a C₁₄ to C₁₅ secondary alcohol with about 10 moles of ethylene oxide.

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