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3,437,598

**CAUSTIC SODA CONCENTRATE**

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5 Claims

This invention relates to concentrates of sodium hydroxide, and more particularly to caustic soda concentrates containing a surfactant.

Caustic soda is widely used in industry in a great variety of applications including industrial cleaning, paint removing, aluminum etching and food treatment. The caustic soda is provided for the user in the form of a concentrate to which water is added to form a more dilute caustic soda solution required for the particular application. Many such caustic soda solutions also contain a small proportion of a suitable surfactant which substantially increases their working efficiency. The solutions such as those employed in industrial cleaning and aluminum etching applications also typically contain a minor portion of sodium gluconate. A typical concentrate as provided to the user contains 40-70% caustic soda and optionally sodium gluconate depending upon the particular application for which it is intended. The user then dilutes with water and adds a surfactant. The requirement that the user add the surfactant has been an unfortunate peculiarity in the industrial use of caustic soda and requires that the user maintain storage and metering facilities for the addition of surfactant. Industrial users of caustic soda have long requested chemical suppliers to provide caustic soda concentrates containing suitable surfactants to eliminate the necessity of the user adding and mixing in this material. Unfortunately, suppliers of caustic soda have been unable heretofore to provide caustic soda concentrates containing a suitable surfactant such that the concentrates could be readily diluted with water to directly form solutions satisfactory for the intended use. The reason for this has been simply that it has been not heretofore possible to find a surfactant which is soluble and stable in the caustic soda concentrates. Thus, those surfactants apparently showing promise have on storage resulted in agglomeration and separation from the concentrates to the extent that the surfactants were not readily redispersible under ordinary conditions of use. In our search conducted over extended periods of time we have investigated numerous materials without success in providing a surfactant for the caustic concentrates. In short, the provision of caustic soda concentrates containing a surfactant and dilutable with water to form caustic solutions suitable for direct use has been a persistent problem heretofore not satisfactorily solved.

An object of the present invention is to provide new and improved caustic soda concentrates.

Another object of the invention is to provide caustic soda concentrates containing a surfactant and readily dilutable with water to provide caustic soda solutions useful as detergents, etchants and in other applications in which such caustic soda solutions are conventionally employed.

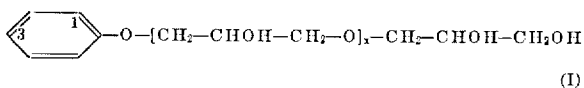
A further object of the invention is to provide caustic soda concentrates containing a surfactant which is both soluble and stable in such concentrates.

Other objects and advantages will be evident from the following description of the invention.

In accordance with the present invention we have found that stable caustic soda concentrates containing a surfactant and dilutable with water for direct use in industrial

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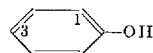
cleaning, aluminum etching and other caustic solution applications are provided by aqueous concentrates comprising 40% to 70% caustic soda, preferably 45% to 55% caustic soda, and between about 0.005% to 1% of a water-soluble adduct of glycidol and an alkylphenol, said adduct having the formula:



in which one of the numbered positions in the benzene ring is occupied by an alkyl group having 8 to 18 carbon atoms, and the other numbered position is occupied by a substituent selected from the group consisting of hydrogen and an alkyl group having 1 to 18 carbon atoms; and wherein x is a value between 4.5 to 25, preferably 4.5 to 12, the ratio of the value of x to the total number of carbon atoms in the alkyl groups at positions No. 1 and No. 3 being at least 0.50.

It has also been found that the above aqueous concentrates are stable in the presence of sodium gluconate which may be added to the concentrates as desired in amounts representing between about 0.5% to 15% by weight of the concentrate, more usually in amounts between 1.0% to 5%. The concentrates of the invention have excellent storability without substantial phase separation and are readily diluted with water upon simple mixing to form caustic solutions containing typically 2% to 20% caustic soda and 10 to 10,000 parts per million of said glycidol-alkylphenol adduct, said diluted caustic soda solutions having substantially improved and high efficiencies in the conventional caustic soda applications by reason of the presence of said glycidol-alkylphenol adduct.

The glycidol-alkylphenol surfactants may be prepared by heating glycidol with an alkylphenol having the formula:



wherein one of the numbered positions in the benzene ring is occupied by an alkyl group having 8 to 18 carbon atoms, preferably 8 to 12 carbon atoms, and the other numbered position is occupied by a substituent selected from the group consisting of hydrogen and an alkyl group having 1 to 18 carbon atoms, preferably hydrogen.

Typical illustrative examples of suitable alkylphenols which can be employed include:

- p-isononylphenol,
- p-isododecylphenol,
- o,p-di-isononylphenol,
- o,p-di-isododecylphenol,
- p-tert-octylphenol,
- o,p-di-tert-octylphenol,
- p-tert-octyl-o-isononylphenol,
- p-tert-octyl-o-isododecylphenol,
- p-sec-octylphenol,
- p-sec-dodecylphenol,
- p-sec-hexadecylphenol,
- p-sec-octadecylphenol,
- o,p-di-doecylphenol,
- p-cetylphenol,
- p-octadecyl-o-cresol,
- p-tert-octyl-o-tert-butylphenol,
- p-isononyl-o-tert-butylphenol,

mixtures thereof, and the like.

The number of moles of glycidol per mole of the alkylphenol to produce water-soluble surfactants useful in the present invention is between 5.5 to 26, preferably between 5.5 to 13.

In preparing the glycidol-alkylphenol adduct it is desirable to add the glycidol to the alkylphenol in order to keep the glycidol from reacting with itself. Therefore, the glycidol is added to the alkylphenol at a rate sufficient to maintain the glycidol concentration in the reaction mass of below about 2 percent, and preferably at about 0.5 percent or less by weight.

The reaction between glycidol and the alkylphenol is preferably carried out in the presence of a catalytic proportion of an alkaline catalyst. Suitable catalysts include the alkali metals and an oxide, hydroxide, alkoxide, or phenoxide thereof. Typical examples of suitable catalysts include sodium, lithium, potassium, sodium hydroxide, potassium hydroxide, sodium methylate, lithium methylate, sodium isopropylate, sodium octadecylate, sodium phenolate, potassium phenolate, sodium cresylate and the like. The catalytic proportion of catalyst is generally between about 0.1 and about 2 percent by weight of the reaction mixture but greater or lesser quantities may be used if desired.

The reaction is carried out at a temperature in the range between about 100° C. and about 200° C., and preferably in the range between about 130° C. and about 160° C.

The time required to complete the reaction will vary with the properties of the reactants, the proportions employed, and the degree of polymerization desired. To illustrate a typical reaction, between about 3 and about 6 hours are required to add to the reactor a total of 6 moles of glycidol per mole of isononylphenol in order to yield a product in which  $x$  is equal to 5. Other time periods can be employed for different alkylphenols or other reaction conditions.

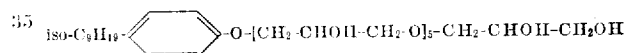
The caustic soda concentrates of the invention may be prepared by any suitable procedure involving mixing of concentrated caustic soda liquor with other components of the concentrate including the glycidol-alkylphenol surfactant, water and other desired ingredients. The caustic soda liquid preferably has a caustic soda concentration between about 40% to 70% by weight approximately corresponding to the desired concentration of the concentrate. When added, the sodium gluconate is preferably incorporated as gluconic acid to form the sodium gluconate in situ. The preferred amount of surfactant is between 0.05% to 5%. In a preferred procedure a 40-70% aqueous solution of the glycidol-alkylphenol surfactant is dissolved with stirring in a 40-70% aqueous solution of gluconic acid in a suitable mixing vessel. The caustic soda may then be added as 40-70% caustic soda liquid slowly with stirring to form a homogeneous mixture. Alternately, caustic soda liquor may be added without stirring to the gluconic acid-surfactant mixture followed by mixing for a short period of time to form a homogeneous solution. Mixing of the ingredients may be generally carried out at room temperature although higher or lower temperature may be employed. Addition of the surfactant directly to caustic soda liquor without prior dissolution in the gluconic acid is less preferred because of the extended mixing time required to form a stable solution surfactant. Other ingredients are not excluded from the concentrates of the invention if properly selected as to compatibility and stability. For example, a defoaming agent may be added although such an additive is not generally required in the concentrates of the invention. The polyalkylene ether polyols are illustrative of materials found to be very suitable as defoaming agents in the concentrates and caustic solutions produced therefrom. Specific examples of such polyalkylene ethers include the propylene based polypropylene oxide diols with molecular weight preferably between 1500 to 3000 and the glycerine based polypropylene oxide triols having molecular weight preferably between 2000 to 4000. The amount of defoaming agent added to the concentrate preferably ranges between about 0.01% to 1.0% by weight of the concentrate.

The following examples in which parts and percentages are by weight illustrate the practice and advantages of the present invention.

#### Example 1

A mixture of 220 g. technical grade para-isononylphenol (1 mole) and 1 g. of potassium hydroxide was stirred in a glass-lined vessel fitted with a rapid agitator and reflux condenser and heated therein under a blanket of nitrogen to 150° C. The para-isononylphenol employed was a technical mixture of isomeric nonylphenols obtained by condensing phenol with tripropylene in the presence of acidic catalysts ( $\text{BF}_3$  and  $\text{H}_2\text{SO}_4$ ). At such temperature ( $\pm 5^\circ \text{C}$ .) pure, dry glycidol was dripped in gradually at such a rate that the glycidol concentration in the mixture was maintained below about 0.5%. The initial feed rate of glycidol to the glass-lined 3 gallon vessel was in the range between about 3.5 to 5.0 g./min./220 g. para-isononylphenol. The rate of reaction was such that about 4.5 hours was required to add a total of 6 moles of glycidol/mole of isononylphenol to give a product where the value of  $x$  was 5 in Formula I. During the course of the reaction additional KOH was added when the total alkalinity in the mixture dropped to below 25% of the original value. When this occurred, an additional 0.75 g. KOH was added for each 220 g. of isononylphenol. At the end of the reaction, a quantity of water equal to the weight of the KOH employed was added. Carbon dioxide gas was introduced until the mixture (after cooling the batch to 100° C.) was below pH 9.

Upon cooling to room temperature a viscous amber-colored water-soluble syrup was obtained, the main component of which had the formula:



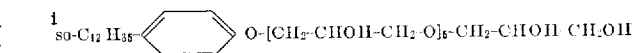
The cloud point of a 1% aqueous solution of this compound was above 100° C. It was important in order to obtain high cloud points that the glycidol reacts with the alkylphenol instead of with itself. This was accomplished in this example by keeping the concentration of free glycidol at a low value at any given moment.

#### Example 2

Example 1 was repeated except that the amount of glycidol was increased such that the mole ratio of glycidol to para-isononylphenol was 10 to 1 and the product had as its main component a glycidol-para-isononylphenol adduct in which  $x$  was equal to 9 according to the Formula I and that given in Example 1.

#### Example 3

In the same manner as described in Example 1, para-isododecylphenol (made from phenol, tertpropylene and  $\text{BF}_3$ ) was reacted at 150° C. with glycidol, using 88.5 g. para-iso-dodecylphenol, 0.24 g. potassium metal, and 173 g. glycidol which was added with agitation over a 3 hour period. The product was a very viscous semi-solid water-soluble material the main component of which had the formula:



The cloud point of a 1% aqueous solution of this compound was greater than 100° C.

Caustic soda concentrates containing 50% caustic soda, 3% sodium gluconate and 0.2% of the glycidol-alkylphenol surfactant prepared by the above examples were prepared by first mixing at room temperature a 50% aqueous solution of the surfactant with 50% aqueous gluconic acid. A homogeneous solution was formed in less than 3 minutes and there was then added thereto at room temperature 50% caustic soda liquor over the course of less than 10 minutes with mixing to form a homogeneous caustic concentrate solution. Each of the

thus prepared concentrates was then placed in a covered container and stored for a period of 8 months at room temperature. Evaluation of each of the concentrates after the 8 months storage showed no signs of degradation or separation of the surfactant demonstrating the excellent stability of the surfactant-concentrates of the invention.

The concentrate prepared in accordance with Example 1, above, and stored for 8 months was evaluated in a simulated typical cleaning application along with a similar but freshly prepared surfactant-caustic soda concentrate, after dilution with 9 parts of water, using as a control a sodium gluconate-caustic soda solution of the same concentration except prepared without the addition of a surfactant. In the cleaning tests a number of glass slides were given a uniform coating of a commercially available casein based waterproof label glue (National Starch 14-9800). The glue was spread over each glass slide with a stirring rod wrapped with two strips of pressure-sensitive tape spaced apart to correspond to the width of the slide to assure the distribution of a similar amount of coating on each slide. In conducting the tests the glue-coated slides were dipped in the caustic solution at a solution temperature of 140° F. at a rate of 20 dips per minute. After the first 10 minutes the slide was removed and sprayed for 5 seconds with water from a squeeze type wash bottle. The procedure of dipping and washing was then repeated using a 5 minute cycle and the time to remove all visible traces of the glue recorded. If, for example, no trace of glue remained at the end of 20 minutes or the third dipping cycle, then cleaning time was recorded as 15-20 minutes. Results are recorded below in the table.

TABLE

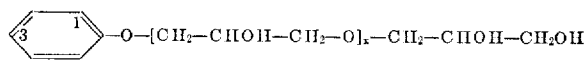
Caustic cleaning solution:	Cleaning time
(A) Freshly prepared concentrate with surfactant of Example 1	20-25
(B) From concentrate with surfactant of Example 1 after 8 months storage	20-25
(C) From control concentrate not containing surfactant	90-95

As shown by the above table, both solutions A and B exhibit about the same cleaning time demonstrating the excellent stability of the surfactant-caustic concentrates of the invention on storage over extended time periods. A comparison of the results obtained with solutions A and B with solution C shows the high degree of effectiveness of the glycidol-alkylphenol adduct in improving the cleaning action of dilute caustic soda solutions.

Although certain preferred embodiments of the invention have been disclosed for purpose of illustration, it will be evident that various changes and modifications may be made therein without departing from the scope and spirit of the invention.

We claim:

1. A stable aqueous caustic concentrate consisting essentially of a homogeneous aqueous solution of 40% to 70% by weight sodium hydroxide and 0.005% to 1.0% by weight of a water-soluble glycidol-alkylphenol adduct having the formula:



in which one of the numbered positions in the benzene ring is occupied by an alkyl group having 8 to 18 carbon atoms, and the other numbered position is occupied by a substituent selected from the group consisting of hydrogen and an alkyl group having 1 to 18 carbon atoms; wherein  $x$  is a value between 4.5 to 25, the ratio of the value of  $x$  to the total number of carbon atoms in the alkyl groups at positions No. 1 and No. 3 being at least 0.50.

2. A caustic concentrate according to claim 1 in which there is also included between 0.5% to 15% by weight of sodium gluconate.

3. A caustic concentrate according to claim 1 in which  $x$  in the formula has a value between 4.5 to 12.

4. A caustic concentrate according to claim 3 in which the alkylphenol is p-isononylphenol.

5. A caustic concentrate according to claim 3 in which the alkylphenol is p-isododecylphenol.

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MAYER WEINBLATT, *Primary Examiner.*

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