Patented Nov. 17, 1942 2,302,598

UNITED STATES PATENT OFFICE

2,302,598

DETERGENT

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No Drawing. Application November 16, 1940, Serial No. 365,944

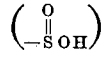
16 Claims. (Cl. 210—23)

This invention relates to water-treating agents, and more particularly to hard water treating agents, for the purpose of converting hard water to water having the inherent advantages of soft water, the invention likewise relating to the agents as detergent assistants.

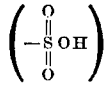
The water-treating agents of the invention may be characterized as detergent assistants, hard-water softening agents, dye assistants, and the like and are employed for the purpose of avoiding or delaying the formation of hard-water precipitates, or alternatively forming precipitates of such nature that they have no deleterious effect on the particular operation of cleaning, dyeing, foaming, or the like.

An object of the present invention is to provide new water-treating agents. A further object of the invention is to provide a process for cleaning textiles, clothes, comestibles, ceramics, and all materials, articles, or products contaminated with fats, oils, dirt, and the like. Another object is to provide highly efficient detergent assistants. Yet another object of the invention is to provide compositions which may be effectively used in dye baths to aid in the dyeing of natural or artificial fibers or fabrics without streaking and/or discoloration due to insoluble metal salts. Other objects and advantages of the invention will hereinafter appear.

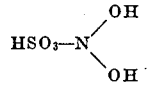
The invention is based on the discovery of new water-treating agents which include the water-soluble derivatives of the series of sulfo acids derived from ortho nitrous acid, $HON(OH)_2$, by the substitution of sulfinic



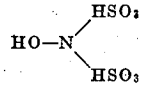
or sulfonic



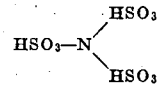
radicals in place of the hydroxyl groups. These sulfo derivatives have the following empirical formulas:



Dihydroxynitrilomonosulfonic acid.

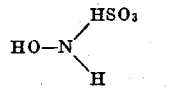


Hydroxynitrilodisulfonic acid.

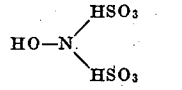


Nitrilotrisulfonic acid.

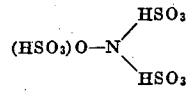
There are likewise included the sulfo derivatives of hydroxyl amine, $HONH_2$, by the substitution of sulfinic or sulfonic radicals in place of hydrogen thereby will be obtained from sulfonic, substitution, acids having the following empirical formulas:



Hydroxynitrilomonosulfonic acid

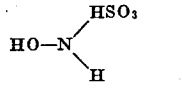


Hydroxynitrilodisulfonic acid.

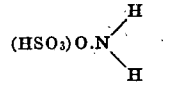


Nitrilodisulfonatemonosulfate.

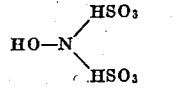
In the case of the mono and disulfonic acids, isomeric forms thereof are likewise possible and these isomeric forms of the acid have the following empirical formulas:



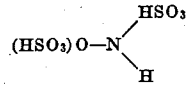
Hydroxynitrilomonosulfonic acid.



Hydroxynitrilo-iso-monosulfonic acid.



Hydroxynitrilodisulfonic acid.



Hydroxynitrilo-iso-disulfonic acid.

Imido disulfonic acid, $HN(SO_3H)_2$, which may be obtained by the hydrolysis of nitrogen trisulfonic acid may be used in the same manner and for the same purposes as the above acids.

It has been found that salts of the above acids and more particularly the water-soluble salts thereof such as the alkali metal salts and the ammonium salts are especially useful as detergents and detergent assistants. One or more of the replaceable hydrogen atoms of the above designated acids may be substituted by a metal to give the corresponding metal salt and likewise in some instances organic esters of these acids and more particularly the alkyl and aryl esters, etherial salts, or inorganic esters, obtained by reacting the acids with alcohols such as methanol, ethanol, propanol and the higher branch and straight chained aliphatic or aromatic alcohols may likewise be employed. As more specific examples of these highly effective detergents and detergent assistants are sodium hydroxynitrilomonosulfonate; mono and disodium hydroxynitrilodisulfonate; mono, di, and trisodium nitrilotrisulfonate; mono and disodium hydroxynitrilodisulfonate; mono, di, and trisodium hydroxynitrilotrisulfonate, monosodium hydroxynitrilomonosulfonate, monosodium hydroxynitrilo-iso-monosulfonate, mono and disodium

hydroxynitrilodisulfonate, and mono and di-sodium hydroxynitrilo-iso-disulfonate.

The above series of acids can be prepared by any suitable process. The following illustrate excellent methods of preparing them:

Potassium nitrilosulfonate

A solution of 25 g. (0.294 M.) KNO_2 dissolved in 100 cc. H_2O is added slowly with stirring to a hot solution of $KHSO_3$ prepared by saturating 75 g. (1.34 M.) of KOH in 150 ml. of water with SO_2. A cloudiness occurs with the formation of a mass of needle-like crystals $N(SO_3K)_3$. After standing 1 hour enough water (1500 ml.) is added to redissolve the crystals on heating. The mass is cooled and filtered, washed with alcohol and ether, then dried.

Potassium iminodisulfonate

38 g. of potassium nitrilosulfonate,

$$N(SO_3K)_3.2H_2O$$

is moistened with 16 cc. of 2% H_2SO_4 solution and let stand 24 hours. The solid product is filtered off, washed with 60 cc. ice water. It is recrystallized from 60 cc. of water containing 10 ml. conc. ammonium hydroxide, filtered, washed with ice water, alcohol, ether and dried.

Potassium hydroxylamine disulfonate

42.5 g. of KNO_2 (0.5 M.) and 54 g. (0.55 M.) of potassium acetate are dissolved in 100 cc. of ice water. 750 g. of cracked ice is added and SO_2 bubbled through until saturated. The temperature is kept below 0° C. The potassium hydroxylamine disulfonate separates from the reaction mixture as a white crystalline material. It is collected on a filter, washed with cold water and dried.

Sodium hydroxyiminodisulfonate

Charge:

$NaNO_2$	4700 g. (67.8 M.)
$NaHSO_3$	7190 g. (69.1 M.)
SO_2	4400 g. (68.8 M.)
Ice	42000 g.
Water	8500 g.

The nitrite and 36.5 kg. of ice is placed in a 17-gal. metal tank fitted with a ½ H. P. "Lightin" mixer and surrounded by an ice-salt mixture maintained at −15° C. The bisulfite is added separately to 8500 g. water and cooled to 2° C. by addition of 5500 g. ice. This mixture, containing some undissolved bisulfite, is saturated with SO_2 and added to the main vessel with agitation; stirring is continued until all ice was broken down into fine pieces. Sulfur dioxide is then run into the reaction mixture for 2¾ hours, until the solution is acid to Congo Red. During this period the temperature is maintained at −5° C. or below. After shutting off the SO_2, agitation is continued for a few minutes to see if the solution remained acid. Hydroxylamine as the di-sulfonate is then recovered.

An excellent discussion of these derivatives of ortho-nitrous acid is given in J. W. Mellor's Treatise on Inorganic and Theoretical Chemistry, vol. VIII, p. 669–684. Extensive original references are cited and the procedure for the preparation of numerous examples is clearly described.

Accordingly, the invention comprises essentially a process involving the addition of the above designated compounds as water-treating agents to water and especially hard water to be used for cleaning, dyeing, and other purposes. Moreover, these agents may be used alone as detergents, in some instances, or combined with detergents as detergent assistants in others. They may be used in either capacity in hard or soft water. More marked effect is noticeable, however, when they are used with hard water. When used with detergents as detergent assistants, a sufficient amount of a base should be present to give a pH of from 9 to 12, i. e., the range in which detergents generally are most effective. These agents may be used in conjunction with a suitable detergent such as, for example, ordinary soaps; that is, the alkali salts of the higher fatty acids. They may also be used with such detergents as the salts of the sulfonic acid derivatives of aliphatic or aromatic hydrocarbons, for instance, alkylated naphthalene sulfonic acids, water-soluble salts of lauryl, cetyl, or oleyl sulfuric acids and like alkyl sulfuric acids, as well as similar salts of condensation products of fatty acids with, for instance, hydroxy acids or aminoalkylsulfonic acids and the like. Other ingredients may also be added, if desired, to the detergent assistant and the detergent, such, for example, as sodium sulfate, sodium carbonate, the silicates, or phosphates together with oxidizing or reducing agents such as the perborates, hydrosulfides, and organic solvents.

These agents if used with detergents may, if desired, be added with the detergent prior to or during the washing operation, or may be added during the final rinsing operation. Such agents may also be previously mixed with the detergent and the resulting mixture then added to the water or the single ingredients may be added in any sequence and in suitable proportions by weight.

While it is possible, by analysis of hard water, to calculate the amount of the agent to be added, this amount in practice can be readily determined by experience in its addition to the point which observation indicates that the calcium and/or magnesium or other metal salts are rendered unobjectionable.

Examples will now be given illustrating by specific embodiments the use and outstanding advantages of the water-treating agents. Unless otherwise indicated, parts given are by weight.

Example 1.—A solution of tallow soap and potassium hydroxynitrilodisulfonate was made up in hard water containing the equivalent of 120 P. P. M. $CaCO_3$, by dissolving 2.0 gm. soap and 0.2 gm. of the disulfonate salt in a liter of the water. This solution was used to wash standard soiled wool crepe in a wash wheel at 120° F. Control tests were run at the same time using 0.2% soap solution in 120 P. P. M. hard water. After rinsing and drying, the swatches washed in the soap solution containing potassium hydroxynitrilodisulfonate were 10 to 20% cleaner than those washed in straight soap solution.

Example 2.—Standard soiled wool crepe was scoured in a wash wheel at 120° F. for 30 minutes in a 240 P. P. M. hard water solution containing 3.0 gm. tallow soap and 0.3 gm. potassium hydroxynitrilodisulfonate per liter. The test was repeated in a solution containing 3.0 gm. soap and 0.6 gm. of the disulfonate per liter. Control tests were run at the same time using 0.3% soap solution in 240 P. P. M. hard water. The deterging of these solutions was evaluated by rating the dried swatches with a photometric reflectometer. By these standards, the solution containing 3.0 gm. soap plus 0.3 gm. potassium hydroxynitrilodisulfonate was equal in deterging to a 0.35% soap solution.

Example 3.—Washing tests with standard soiled wool crepe in 120 P. P. M. hard water were repeated as decribed in Example 1 but using sodium hydroxynitrilodisulfonate as builder in place of potassium hydroxynitrilodisulfonate. A soap saving of about 50% was indicated by photometric comparison of the washed cloths.

Example 4.—A solution containing 2.0 gm. soap and 0.2 gm. potassium imidodisulfonate in one liter of 120 P. P. M. hard water was used to wash standard soiled cloth at 120° F. in a wash wheel. Control runs were made at the same time with soap solutions in 120 P. P. M. hard water containing 2.0 gm. and 3.0 gm. soap per liter respectively. After washing, the swatches were rinsed, dried, and rated photometrically for comparative whiteness. Cloth washed in the soap solution containing the imidodisulfonate was as clean as that from the 0.3% soap solution without builder.

Example 5.—Standard soiled muslin was scoured in the wash wheel at 130° F. for 30 minutes in solutions as follows:

Test	Hard water	Grams soap/liter	Grams builder/liter
	P. P. M.		
1	120	2.0	None
2	120	1.6	0.4 $HON(SO_3K)_2$
3	120	1.6	0.3 $HON(SO_3K)_2$ 0.05 Na_2CO_3 0.05 Na_2SO_4
4	240	2.5	None
5	240	2.0	0.5 $HON(SO_3K)_2$
6	240	2.0	0.32 $HON(SO_3K)_2$ 0.085 Na_2CO_3 0.095 Na_2SO_4

After washing, the swatches were rinsed, dried and rated photometrically. Comparative ratings were as follows:

Test No.—	Rating
1	100
2	98
3	100
4	100
5	93
6	102

These results indicate that 20% of the soap can be substituted by $HON(SO_3K)_2$ as a builder without impairing the detergency efficiency of the wash solutions.

The water-treating agents may be used for, in addition to the uses described above, wetting out of gray goods, assistant in peroxide bleaching, scouring rayon yarns and fabrics, wetting out of cotton goods that are to be pre-shrunk, scouring of lime-pulled wool, degumming, preparation of raw stock for dyeing, as a dispersing and penetrating agent in dyeing, penetrating agent in warp sizing, and in alkaline fulling.

In the appended claims "normal industrial use" of water treated with the compounds herein disclosed will include its use in deflocculating, foaming, deterging, penetrating, dyeing, wetting and scouring.

They may also be used, preferably with a detergent, in removing grease from other grease-laden articles. For example, the palm oil used in the cold-rolling of steel sheets may be removed by scrubbing the sheets with hot water containing a detergent and the treating agent. A similar bath may be used for the washing of parts prior and/or subsequent to electroplating, painting, lacquering, finishing, and the like.

I claim:

1. In a process involving the treatment of water, whereby its use for flocculating, deflocculating, foaming, deterging, dyeing and wetting will be more effective, the step which comprises introducing into the water a water-soluble salt of a hydroxynitrilosulfonic acid.

2. In a process involving the treatment of water, whereby its use for flocculating, deflocculating, foaming, deterging, dyeing and wetting will be more effective, the step which comprises introducing into the water a water-soluble salt of a hydroxynitrilopolysulfonic acid.

3. In a process involving the treatment of water, whereby its use for flocculating, deflocculating, foaming, deterging, dyeing and wetting will be more effective, the step which comprises introducing into the water a water-soluble salt of a hydroxynitrilodisulfonic acid.

4. In a process involving the conversion of hard water to water having the inherent advantages of soft water, the step which comprises effecting said conversion by the introduction of disodium hydroxynitrilodisulfonate.

5. In a process involving the conversion of hard water to water having the inherent advantages of soft water, the step which comprises effecting said conversion by the introduction of sodium imidodisulfonate.

6. In a process involving the conversion of hard water to water having the inherent advantages of soft water, the step which comprises effecting said conversion by the introduction of sodium hydroxynitrilosulfonate.

7. In a process involving the conversion of hard water to water having the inherent advantages of soft water, the step which comprises effecting said conversion by the introduction of potassium nitrilotrisulfonate.

8. In a cleaning process involving the use of a bath containing hard water and a detergent, the step which comprises introducing into the bath a sodium salt of a hydroxynitrilosulfonic acid.

9. In a process involving the treatment of water, whereby its normal industrial use will be more effective, the step which comprises introducing into the water a water-soluble sulfo derivative of an ortho nitrous acid.

10. In a process involving the treatment of water, whereby its normal industrial use will be more effective, the step which comprises introducing into the water a water-soluble derivative of a hydroxy-substituted nitrilo sulfonic acid.

11. The process of claim 10 in which a metal salt of the acid is used.

12. The process of claim 10 in which an alkali metal salt of the acid is used.

13. In the use of a dye bath, in which hard water under precipitate forming conditions is employed, the step which comprises adding to the dye and the hard water a water-soluble salt of a hydroxy-substituted nitrilo sulfonic acid.

14. As a composition of matter an alkaline cleaning bath containing a water-soluble salt of a hydroxy-substituted nitrilo sulfonic acid.

15. As a composition of matter an alkaline cleaning bath containing soap and potassium hydroxy-nitrilo disulfonate.

16. As a composition of matter an alkaline cleaning bath containing soap and potassium hydroxynitrilo disulfonate present in the ratio of approximately two grams of soap to 0.2 gram of the potassium hydroxybitrilo disulfonate per liter of water.

WALTER M. BRUNER.