United States Patent Office

2,863,837
Patented Dec. 9, 1958

2,863,837

CORROSION INHIBITING BATH

Bernhard Kowald, Opladen-Lutzenkirchen, and Gunther Tischbirek, Dusseldorf-Holthausen, Germany, assignors to Henkel & Cie. G. m. b. H., Dusseldorf-Holthausen, Germany

No Drawing. Application May 4, 1956
Serial No. 582,658

Claims priority, application Germany May 7, 1955

2 Claims. (Cl. 252—394)

It has been found that sulfonation products of nitriles, particularly nitriles of higher molecular fatty acids, act as corrosion inhibiting agents for iron, aluminum, zinc and the alloys thereof, more particularly in aqueous solutions of substances with which the metals can react under formation of hydrogen.

Nitriles, from which the corrosion inhibitors according to the invention can be made, may be derived from saturated or unsaturated, straight-chain or branched fatty acids containing 6–20, preferably 10–18, carbon atoms per molecule. The nitriles may be substituted by various methods with sulfo groups, for instance by reaction with concentrated, i. e. 95–100% sulfuric acid, or with sulfonating agents, having a higher effectiveness than concentrated sulfuric acid, e. g. oleum, chlorosulfonic acid, sulfur trioxide etc. The sulfonation may be carried out in the presence of solvents which should preferably be inert with respect to the sulfonating agents used. The method described in German Patent 907,053 dealing with the sulfoxidation of nitriles also yields useful sulfonation products of the same.

The structure of the sulfonation products obtained from carboxylic acid nitriles differs according to the sulfonation methods applied. Not always will the nitrile group be preserved during the sulfonation process; however, the presence of non-polar nitrogen, that is to say, nitrogen which is not salt-forming, is a necessary condition for the protective action against corrosion.

Such action will be effective in systems containing iron, aluminum, zinc and solutions of substances which may react with the above mentioned metals under formation of hydrogen. The inhibitive action will not only occur in solutions where a concentration of the dissolved substance evolving hydrogen with the metal is high enough to result in evolution of hydrogen spontaneously, it will also prevail in diluted solutions, in which the metal would only be attacked in the course of a prolonged contact between metal and solution. Consequently, the sulfonation products of nitriles act as inhibitors against acid attack and as protective agents against corrosion. By inhibitors against acid attack we understand compounds which prevent spontaneous evolution of hydrogen or decrease the same; by protective agents against corrosion we understand agents capable of counteracting a slow attack on the metal which would only be noticeable after a longer period.

Both groups of substances may be called anti-corrosives. The concentrations of the anti-corrosives which are to be applied, depend on the metal, the attacking liquid, the temperature, the sulfonation process used, and the molecular size of the nitriles. Minimum concentrations of the anti-corrosives are at about 0.01%. Usually, higher concentrations will be employed, e. g. 0.05–0.5%. More than 1% will only be used in special cases.

Although it is already known to use aromatic nitriles as corrosion inhibitors, it will be seen from the comparison tests described in Example 1 that the effectiveness of the substances used according to the invention is not only due to the presence of the nitrile group, but is obviously specific to the sulfonated nitriles. The presence of non-polar nitrogen is necessary for the inhibiting action as may be seen from the inefficiency of sulfonated fatty acids prepared by hydrolysis of the nitrile group of a sulfonated nitrile.

It is particularly surprising that the corrosion inhibitors according to the invention may be used as well in acid as in alkaline solutions. Due to their wetting properties, the sulfonated nitriles of the invention will cause a satisfactory wetting of metal surfaces by the treated solution. They will also cause a coating layer of lather in treatment baths such as mordant baths, such action being sometimes desirable because it counteracts the formation of mordant mist.

The invention will now be more fully described in a number of examples, but it should be understood that these are given by way of illustration and not of limitation, and that many changes in the details can be made without departing from the spirit of the invention.

METHODS OF PREPARING SULFONATION PRODUCTS OF FATTY ACID NITRILES

(1) About 0.4 mol. of a fatty acid nitrile are dissolved in 100 ml. perchloro ethylene at room temperature, and added thereto is a solution of 22 g. sulfur trioxide in 150 mm. perchloro ethylene. The reaction vessel is cooled from the outside with tap water. After the reaction is completed, the mixture is passed into a dilute sodium hydroxide solution, and the solvent is separated. The aqueous phase is evaporated, and we obtain a solid colorless salt which lathers profusely in aqueous solution.

(2) 162 kg. bromine are added to 260 kg. stearic acid nitrile which is heated to 105–106° C. in the presence of sulfur as a catalyst. The slightly exothermic reaction proceeds rapidly. After introducing the bromine, the reaction is allowed to continue for a certain time, whereafter HBr is driven off. 346 kg. of the brominated product are heated to 100–105° C. with a solution of 320 kg. Na_2SO_3 for 60 hours, while stirring vigorously. A paste is thus obtained which contains the sodium sulfonate of the stearic acid nitrile. The paste can be used as is or after dilution, or after drying to powder. By treating the mass with solvents, for instance with butyl alcohol, the sulfonate can be separated from mineral salts and may be then used for the purpose of the invention.

(3) 350 parts b. w. of lauric nitrile are treated with 20,000 parts by vol. SO_2 and 10,000 parts by vol. O_2 p. hour in a quartz apparatus for 4 hours with U. V. light. The mixture yields upon extraction with water, neutralization of the aqueous solution with NaOH, and evaporation, 160 parts b. w. of a salt mixture containing 95% sodium salt of lauric nitrile monosulfo acid.

(4) Another method of preparing the sulfonated nitrile is to take 1 molecular weight in grams of any of the following acid nitriles: the nitrile of caproic, caprylic, pelargonic, capric, lauric, myristic, palmitic or stearic acid, and dissolve it in 500 cc. CCl_4 and mix with the equimolecular amount of chlorosulfonic acid. The whole is refluxed until gas evolution has ceased. Then the solvent is distilled off, leaving behind the desired sulfonation product of the fatty acid nitrile.

In the following examples, the number given after the fatty acid nitriles corresponds to the above numbers of the methods of preparation.

Example 1

Cold-rolled iron sheets with well polished surface are placed into 20% H_2SO_4 of 60° C. for 1 hour. To the

sulfuric acid, the preparations of Table 1 are added in the amounts there indicated. The last column of the table shows the efficiency in percent of the attack effected by sulfuric acid without any addition.

The sulfonated coconut-fatty acid is the product of hydrolysis of coconut nitrile sulfonic acid (1).

TABLE 1

Added Agent	Quantity in percent	Inhibitor Efficiency in percent of pure H_2SO_4
Benzonitrile	0.05	55
Acetonitrile	0.05	8
Nitrile of a fatty acid C_{12}	0.05	33
Nitrile of a fatty acid C_{16}	0.05	15
Sulfonated coconut fatty acid	0.05	5
Sulfonation product (1) of the nitrile of C_{16} fatty acid	0.05	89
Sulfonation product (1) of the nitrile of C_{16} fatty acid	0.017	80
Sulfonation product (1) of the nitrile of coconut fatty acid	0.05	85
Sulfonation product (2) of the nitrile of coconut fatty acid	0.05	76
Sulfonation product (3) of the nitrile of coconut fatty acid	0.05	73

Example 2

Treatment of zinc in 1 n HCl for 1 hour

TABLE 2

Added Agent	Quantity, percent	Temp., ° C.	Inhibitor Efficiency
Sulfonation product (2) of the nitrile of C_{12} fatty acid	0.1	25	96
Do	0.1	60	99
Do	0.01	25	89
Sulfonation product (1) of the nitrile of C_{12} fatty acid	0.1	25	95
Do	0.1	60	96
Sulfonation product (1) of the nitrile of coconut fatty acid	0.1	25	94
	0.1	60	97
	0.05	60	77
	0.01	25	78
Sulfonation product (2) of the nitrile of coconut fatty acid	0.05	60	97
Sulfonation product (4) of the nitrile of coconut fatty acid	0.05	60	91

The last column of the table shows the efficiency in percent of the attack effected by 1 n HCl without any addition.

Example 3

Treatment of aluminum in 1 n HCl for 1 hour

TABLE 3

Added Agent	Quantity, percent	Temp., ° C.	Inhibitor Efficiency
Sulfonated product (2) of the nitrile of C_{12} fatty acid	0.1	25	99.2
Do	0.1	60	99.2
Do	0.01	25	98
Do	0.01	60	83
Sulfonation product (1) of the nitrile of C_{12} fatty acid	0.1	25	99.5
Do	0.1	60	99.5
Do	0.01	60	58
Sulfonation product (3) of the nitrile of coconut fatty acid	0.1	25	99.2
Do	0.01	25	96
Do	0.01	60	82
Sulfonation product (1) of the nitrile of coconut fatty acid	0.01	25	70–90

The last column of the table shows the efficiency in percent of the attack effected by 1 n HCl without any addition.

Example 4

Treatment of aluminum in 0.25 n NaOH for 1 hour

TABLE 4

Added Agent	Quantity, percent	Temp., ° C.	Inhibitor Efficiency
Sulfonated product (1) of the nitrile of coconut fatty acid	0.05	60	95
C_{12}–C_{18} Alkyl sulfate	0.05	60	15

Inhibitor efficiency in percent of 0.25 n NaOH without addition.

Example 5

(Change of inhibitor action with time of heating in acid bath in the presence of an anti-corrosive)

TABLE 5

Metal	Bath	Inh.	Temp., ° C.	Period of Treatment, hr.	Effectiveness, percent
Al	0.25 n NaOH.	0.05% Sulf. (1) pr. nitrile coconut f. a.	60	1	95
	0.25 n NaOH.	do	60	18	97
Fe	4n H_2SO_4	0.05% Sulf. pr. (2) Nitrile C_{12} f. ac.	60	1	76
	4n H_2SO_4	do	60	18	83
Fe	4n H_2SO_4	0.05 S. p. (1) Nitrile coconut f. a.	60	1	78
	4n H_2SO_4	do	60	18	87

Effectiveness of inhibitor in last column is given in percent of solvent without addition.

What we claim is:

1. A bath for treating metals in order to protect them against corrosion, wherein the metals treated are selected from the group consisting of iron, zinc, aluminum and the alloys of said metals, said bath containing an aqueous solution of a substance capable of evolving hydrogen in the presence of said metals and as an anticorrosive a sulfonation product of a nitrile of a fatty acid having from 10–19 C atoms per molecule.

2. A process for protecting metals selected from the group consisting of iron, zinc, aluminum, and the alloys of said metals, against corrosion in liquids containing substances capable of evolving hydrogen in the presence of said metals, which comprises adding to said liquids a sulfonation product of a nitrile of a fatty acid having from 6–20 C atoms per molecule, in an amount ranging from 0.01–0.1% by weight of the liquid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,411,593 Routson ---------- Nov. 26, 1946

FOREIGN PATENTS

907,053 Germany ---------- Mar. 12, 1954