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USING LACTAMIC SULFATE TO CLEAN AND REMOVE DEPOSITS

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ABSTRACT OF THE DISCLOSURE

Process for cleaning and removing deposits and formations on various substrates and surfaces by the use of lactamic sulfate.

This invention relates to a process for cleaning and removing deposits and formations from various substrates and surfaces.

The problem of deposits and formations on various substrates and surfaces has long been particularly troublesome in processing equipment employed in the chemical, oil, food, beverage, mineral products, metal fabricating, and water processing industries. These deposits and formations, especially, for example, carbonates, sulfates, oxalates, hydroxides, and oxides, which build up on products and equipment used in these industries frequently cause interruptions in production and in service in order to clean the products and equipment and to remove such deposits and formations. Where water is utilized in a process, the problem encountered with carbonate and sulfate deposits and formations may be minimized or reduced to a certain extent by pretreatment of the water. In spite of this, deposits and formations in equipment such as evaporators, heat exchangers, boilers, particularly marine boilers, high pressure boilers, power generating equipment, and the like, and equipment used in breweries, dairies, oil wells, etc. are still encountered and necessitate a shut-down in service for cleaning.

The problems of deposits and formations is also especially acute in the manufacture, processing, and fabrication of metals, particularly iron and steel. While carbonates and sulfates form as deposits on metal surfaces and substrates, oxides are especially troublesome. Descaling and pickling of metals, particularly iron and steel, have long been recognized as effective methods for the removal of surface oxides.

Descaling is sometimes defined as a process in which metallic oxides are exposed to or treated with an acid or a strong reducing agent. Descaling is also defined herein as a process in which an unwanted deposit of a foreign substance is removed from a substrate or surface. Most metals and alloys may be treated by such a descaling process. The advantages of descaling with a reducing agent are that after the reducing reaction, no further attack on the base metal takes place and cleaning of metals and alloys during fabrication is thereby expedited. Descaling with a reducing agent is also considered more advantageous than pickling since pitting of the base metal or alloy seldom occurs during descaling and overtreatment of the work material is usually precluded. Losses ordinarily encountered with pickling are eliminated since there is no attack on the base metal in the descaling bath.

Pickling is the most widely used treatment for the surface of iron and steel products because of its low cost and is defined as the chemical removal of scale and surface oxides from a metal by immersion of the metal in an acid solution during its manufacture, processing, and fabrication. The type, strength, and temperature of the acid solutions used permits wide variations in the pickling process. Moreover, the pickling procedure depends upon

the metal to be pickled and the surface desired after pickling.

While sulfuric, muriatic, nitric, or hydrofluoric acids or mixtures are generally used for descaling and pickling, sulfuric acid is especially preferred because it is the cheapest. Nuriatic, nitric, and hydrofluoric acids are ordinarily used for special descaling and pickling purposes. In recent years, sulfamic acid has found wide acceptance as a descaling acid.

In the descaling or pickling of metals, the concentration of the pickling acid and the pickling temperature are extremely important since attack of the base metal may result unless certain control of these variables is maintained. To prevent attack of the base metal, pickling inhbiitors, agents which may be added to an acid pickling bath to diminish the attack of acid on areas from which the scale has been removed without appreciably retarding the rate of removal of oxides, have found increasing acceptance. Advantages of pickling inhibitors are seen in the reduction of metal loss, saving of pickling acid, prevention or minimizing of scrap losses from overpickling and decrease in blistering and hydrogen embrittlement. The disadvantages of inhibitors are increased pickling times, possibility of residual surface film, and added cost of the inhibitor.

It is an object of this invention to provide a process whereby deposits and formations on various surfaces and substrates may be easily cleaned and removed.

It is a further object of this invention to provide a process for cleaning and removing sulfate, carbonate, oxalate, hydroxide, and oxide deposits and formations from various surfaces and substrates.

It is a still further object of this invention to provide a process for cleaning and removing deposits and formations from various surfaces and substrates employing a novel cleaning, descaling, and pickling agent, the use of which overcomes many of the disadvantages inherent in agents known for such purposes.

It is a still further object of this invention to provide a process for the cleaning and removing of salts, scale, rust, etc., from processing equipment and surfaces of metal, glass, etc.

It is an additional object of this invention to provide a process wherein an economical cleaning, descaling, and pickling agent having a slower rate of attack on metal substrates thereby ordinarily reducing the need for the use of inhibitors in combination with such agent.

It is an added object of this invention to provide a process for cleaning, descaling, and pickling using an easily handled, low cost agent for such purposes.

In accordance with the present invention, realization of the foregoing objects is obtained and the disadvantages of prior methods are substantially overcome by a process for cleaning and removing deposits and formations from various surfaces and substrates employing lactamic sulfate.

Lactamic sulfate, a cream-colored crystalline solid having a melting point of 160° C. (dec.) is an ester of lactamide, obtained from lactonitrile and sulfuric acid. Lactamic sulfate is highly ionized in water solution, is non-volatile, and is especially useful in applications where precipitation of insoluble salts is to be avoided. While lactamic sulfate may be considered to be an old compound, its synthesis having been alluded to in J. Verhulst, Bull. Soc. Chem. Belg., 39, 563 (1930), and 40, 475 (1931), and also in Crawford, J. Soc. Chem. Ind., 64, 231 (1945), its use as a cleaning, descaling, and pickling agent has not previously been described.

Lactamic sulfate may be readily prepared from lactonitrile and sulfuric acid using certain critical mole ratios of the reactants and certain critical temperature and processing conditions as described and claimed in a copending application Ser. No. 350,075, filed Mar. 6, 1964,

of one of us, Richard Parke Welcher, filed concurrently herewith.

While other mineral acids such as sulfuric, muriatic, nitric, and hydrofluoric have been used for cleaning, descaling, and pickling, their use has been hampered to a large extent because of problems encountered after the deposits or formations have been removed. Frequently, destruction or attack of the substrate has resulted. As pointed out previously, inhibitors have been employed so as to prevent or to minimize such destruction or attack.

Sulfamic acid, unlike the just mentioned mineral acids, is a solid acid and because of such property has considerable advantages from the point of view of ease of handling. However, sulfamic acid has a fast rate of attack much like the mineral acids and on account of this, an inhibitor is also used in sulfamic acid cleaning, descaling, and pickling baths and formations.

The use of lactamic sulfate, by contrast, is noted to offer exceptional advantages over the mineral acids and sulfamic acid. Thus, it has been unexpectedly found that it has a much slower rate of attack upon the substrate whose surface is to be cleaned, descaled, or pickled. Because of this unusual characteristic, the use of an inhibitor in the cleaning, descaling, or pickling bath is generally not required. Since an inhibitor is not ordinarily required, shorter pickling and simpler, lower-cost formulations are possible. However, inhibitors as well as surface active agents, builders and fillers may be incorporated in a formation or bath of lactamic sulfate in a specific application.

Lactamic sulfate may be used as a cleaning, descaling, and pickling agent in the treatment of a variety of surfaces and substrates wherein carbonate, sulfate, oxalate, hydroxide, and oxide deposits and formations are troublesome. Thus, for example, it is especially valuable for the surface treatment of metals, particularly iron and steel. However, other surfaces and substrates which may be cleaned and deposits and formations removed therefrom include inter alia, glass, porcelain, ceramic, plastic, textiles, paper, and the like.

The concentration of lactamic sulfate to be used in cleaning, descaling, or pickling applications may be varied over a wide range: from about 1% to about 75%, by weight. Ordinarily, concentrations about 10% of lactamic sulfate, by weight, are employed. However, the concentration used depends upon the temperature of the lactamic sulfate solution, type of materials being cleaned, descaled, or pickled, and the surface desired. For example, when used on certain mild steels, the optimum concentration of lactamic sulfate is about 5 to 10%. For the cleaning and descaling of heavy deposits from tubes and pipes, a higher lactamic sulfate concentration is ordinarily maintained since solution on the inside of the tubes and pipes does not circulate readily.

The temperature employed during cleaning, descaling, and pickling may be varied over a wide range. Generally, temperatures of from about 60° to about 200° F. are employed.

Techniques customarily employed for cleaning, descaling, and pickling may be readily adapted to the process of the present invention using lactamic sulfate. Thus, cleaning, before pickling, may be advisable particularly where a metal such as, for example, iron or steel, to be pickled is covered with grease from previous fabricating processes. Since the grease is not soluble in acid and renders pickling difficult, hot alkaline solutions may be used to remove the grease. Also, following cleaning, descaling, and pickling, thorough washing and treatment of the surface or substrate with water and/or alkali is recommended. Residual lactamic sulfate not rinsed or removed from the metal may possibly promote rusting of iron or steel when the same is exposed to air. A water or an alkaline rinse may be used to remove traces of lactamic sulfate after a water rinse. Such alkaline rince may be made of ½% caustic soda and ¾% of trisodium phosphate. Alternatively, a cold dip in lime is also effective for neutralizing trace amounts of lactamic sulfate.

It is also surprisingly noted that the use of lactamic sulfate as a pickling agent is remarkably effective in minimizing defects such as overpickling, pickle pitting, blistering, and hydrogen embrittlement ordinarily encountered with other pickling agents. Since lactamic sulfate has a slower rate of attack on the base metal, overpickling which causes porosity and roughening of surfaces may be avoided. The use of lactamic sulfate having a low rate of attack also reduces or eliminates the necessity for the use of inhibitors which are customarily employed with mineral acids in order to prevent overpickling.

Blistering and hydrogen embrittlement appears to take place from hydrogen generated during the pickling operation. With lactamic sulfate having a slower rate of attack on the base metal, these defects may be minimized.

While the use of lactamic sulfate in still pickling methods is generally perferred, it is also possible to employ lactamic sulfate in electrolytic pickling techniques. Electrolytic pickling is usually much more rapid than still pickling because of the greater evolution of hydrogen during electrolytic pickling which agitates the pickling solution, reduces scale, and tends to pry off scale from the surface of the metal. Thus, lactamic sulfate may be readily substituted from sulfuric acid which is commonly used in such electrolytic pickling processes.

In order to further illustrate the present invention, the following examples are given:

EXAMPLE 1

Cleaning of carbonate and sulfate deposits

Scale deposits are prepared by evaporating 200 cc. suspensions of water containing 0.5 g. of calcium carbonate and 1.0 g. of calcium sulfate. Such deposits are typical of those found in evaporators or boilers. The scale formed by evaporation of these suspensions is dissolved and disintegrated readily on treatment with a 1% solution of lactamic sulfate.

EXAMPLE 2

Removing of oxide formations

(a) Two-inch-long samples of pipe are cut from a length of rusty ⅝" ID iron pipe. Ten percent (wt./wt.) solutions of lactamic sulfate and sulfamic acid in water are prepared and labelled A and B, respectively. Each solution has an initial pH of 0.05 indicating equivalent acid strength. When the pipe samples are immersed in solutions A and B at room temperature (70° F.), solution B, containing sulfamic acid, immediately attacks the freshly-cut bare metal ends of the pipe as shown by evolution of gas. Solution A, containing lactamic sulfate, shows no gas bubbles.

(b) The pipe samples are removed and both solutions are heated to 150° F. The pipe samples are then immersed for fifteen minutes while maintaining the solution temperature at 150–170° F. During this time, solution B, containing sulfamic acid, strongly attacks the bare metal end of the pipe sample, as shown by vigorous evolution of gas. Solution A attacks the bare metal at a much slower rate with only a few bubbles of evolving gas. The pipe samples are removed from the bath, rinsed in cold water and acetone, dried and inspected. Sample A, cleaned in lactamic sulfate solution A shows an overall change of color from dark brown to light brown, indicating an even, substantial removal of rust. There are more than a dozen areas (2–3 mm.^{2}) from which all rust is removed. Sample B, cleaned in sulfamic acid solution B, still has a splotchy appearance with a few areas of bare metal the size of a pin-head. The inside of sample A is completely free of rust; sample B shows several rusty spots.

(c) Both solutions are reheated to 170–180° F. and the pipe samples reimmersed for 1.25 hour with occasional visual inspection of the pipe. During this time, as more rust is removed from the samples, an increasing amount

of bare metal substrate becomes visible. The evolution of gas from the metal substrate in solution B, containing sulfamic acid, becomes so vigorous as to dislodge rust physically from the metal. In solution A, containing lactamic sulfate, attack on the metal substrate continues to be slow.

At the end of the heating period, both samples are rinsed and dried as in (a) and (b), above. Both samples are now almost completely free of rust. Sample A, cleaned in lactamic sulfate is almost entirely clean, having only a dozen spots of rust each the size of a pin-head. Sample B, cleaned in sulfamic acid, had a patch of rust 2 mm. in diameter. There is also a significant difference in the appearance of the metal surface. Sample A, cleaned in lactamic sulfate is light gray and smooth in appearance, and shows metal crystal structure. Sample B, cleaned in sulfamic acid, has a dark gray, sooty, pitted appearance. When rubbed with the finger, sample B leaves a sooty mark on the finger. These observations are confirmed by photomicrographs.

From the foregoing examples, it will be readily apparent that lactamic sulfate is a markedly effective and efficient agent for cleaning and removing deposits and formations of various kinds, for example, carbonate, sulfate, and oxide types. Example 2 readily points up the surprising advantages of lactamic sulfate over a commerically available solid acid, sulfamic acid, in the descaling and pickling of metals, especially ferrous metals. Thus, the results of (a), (b), and (c) of that example clearly indicate that lactamic sulfate is a superior pickling agent in three respects: it attacks the oxides, i.e., rust, more quickly, consumes the bare metal more slowly, and leaves the metal with a smoother surface.

While the foregoing invention has been described in conjunction with various preferred embodiments, it is to be understood that the invention is not to be solely limited thereto but is to be construed broadly and restricted only by the appended claims.

We claim:

1. A process for cleaning and removing deposits and formations from a substrate comprising treating said substrate with lactamic sulfate.

2. A process for cleaning and removing deposits and formations from a substrate comprising contacting said substrate with lactamic sulfate.

3. A process for cleaning and removing deposits and formations of a compound selected from the group of carbonates, sulfates, oxalates, hydroxides, and oxides from a substrate comprising treating said substrate with lactamic sulfate.

4. A process for cleaning and removing deposits and formations of a compound selected from the group of carbonates, sulfates, oxalates, hydroxides, and oxides from a substrate comprising contacting said substrate with lactamic sulfate.

5. A process for the surface treatment of a metal comprising descaling and pickling said metal with lactamic sulfate.

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