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PICKLING BATH FOR METALS

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This invention relates to improvements in the pickling of metals and more particularly to pickling inhibitors, i. e., materials which retard the rate of reaction of aqueous acid on metals, as in pickling steel. The invention includes not only the improvements in pickling, but also new pickling baths containing the inhibitors.

Inhibitors used in accordance with the invention are sulfur derivatives of higher aliphatic amines and other nitrogen bases, resulting from the chemical combination of sulfur or a sulfur compound in which the sulfur has a valence lower than six, including sulfur, the polysulfides, sulfur dioxide, sulfurous acid and its salts, carbon bisulfide, mercaptans, organic sulfides and disulfides, thionyl chloride and other sulfur chlorides, salts of thionic acids, hyposulfurous acid, thiosulfurous acid, and the like, with higher aliphatic amines or nitrogen bases, including in particular those prepared by amination of chlorinated hydrocarbons.

The nitrogen compositions which may be combined with sulfur or one of its lower valence compounds in producing the new compositions are the aminated products resulting from the direct amination of chlorinated aliphatic hydrocarbons such as gasoline, kerosene, gas oil and paraffin with ammonia.

Products resulting from the treatment of these amines, and particularly the product resulting from the amination of chlorinated kerosene, as described in my application Serial No. 382,211, filed March 7, 1941, with sulfur or sulfur dioxide, give outstanding results as pickling inhibitors. The amines from various chlorinated petroleum fractions such as gasoline, kerosene, gas oil or paraffin may be employed, either directly as the crude product resulting from the amination, or as products purified by distillation or other known methods of purification, or as the residues resulting from the distillation of such products. Any of these materials form highly active pickling inhibitors when combined with sulfur in a low valence state, and may be used with advantage in practicing this invention.

It requires only a trace of sulfur (or sulfur compound) to impart to these amines pronounced inhibitor activity, although in general the quantity of sulfur or sulfur compound used will be appreciable. For example, if a small amount of one of the amines, say a fraction of 1%, is dissolved in a typical acid pickling bath, and is then treated with but a trace of a soluble low valence sulfur compound, the action of the acid on steel or iron is markedly inhibited. Thus the addition of sulfur dioxide, sodium sulfide, bisulfite, hyposulfite, thiosulfite, hydrosulfide or hydrogen sulfide or the polysulfides to a bath containing one of these amines gives good results.

In general, however, it is simpler and more satisfactory to form an amine-sulfur product separately and add it to the pickling solution.

The invention will be illustrated by the following specific examples, but it is not limited thereto.

Example 1.—284 parts of the crude amines resulting from the amination of a chlorinated Michigan kerosene containing chlorine as described in my said application Serial No. 382,211, were treated with 82 parts of sulfur dioxide, forming 366 parts of reaction product. The amine, which had a molecular weight of about 250, combined with the sulfur dioxide in the ratio of 1 to 1.13. The reaction was exothermic and considerable heat was given off. The reaction was assumed to be completed when the evolution of heat stopped. The product was a dark viscous oil, soluble in water and having a slight odor of sulfur dioxide. Addition of alkali liberated the amines. The product was soluble in dilute aqueous acid. Tested by standard procedure, in a 6% sulfuric acid pickling bath, this product showed a high inhibiting efficiency. This same product, dissolved in a pickling bath containing 15% hydrochloric acid again gave excellent results in inhibiting loss of metal.

Example 2.—Hydrogen sulfide was passed into 25 parts of the amine described in Example 1 until 3.5 parts of the hydrogen sulfide were absorbed, corresponding to a molecular ratio of 1:1. The reaction was somewhat exothermic. The product was a black viscous oil with an undesirable odor, unstable toward alkali, and somewhat soluble in water and dilute aqueous mineral acids. It was a good pickling inhibitor for either sulfuric or hydrochloric pickling baths.

Example 3.—28 parts of the amine of Example 1 were mixed with 3.6 parts of flowers of sulfur and allowed to stand for several hours. The sulfur dissolved completely, giving a black viscous oil somewhat soluble in water and dilute aqueous mineral acids and having a high inhibiting efficiency in acid pickling baths. Very little heat was generated when the amines combined with the sulfur.

Other products, which, with various sulfur compounds such as those referred to above, give pickling inhibitors of high efficiency, include the fraction resulting from the distillation of a crude amine from chlorinated kerosene at 110–180°

C./15 mm., a fraction of the same amine boiling at 48–107° C./18–20 mm., and another fraction of the same amine boiling at 192–208° C./15–16 mm.

It is not necessary that the sulfur be combined with the amine after the amine is produced. In some cases, effective inhibitors may be directly produced from petroleum fractions, such as Michigan kerosene, which contain a small amount of combined sulfur. This is illustrated by the following example:

Example 4.—A crude amine resulting from the amination of a chlorinated Michigan kerosene containing some sulfur was heated, in the form of the sulfate, at 200° C. for five hours. The resulting product had excellent inhibiting efficiency. The same amine, without heating or conversion to the sulfate, was subjected to vacuum distillation giving a distillate boiling at 115–175° C./15 mm. and a residue. The distillate had a relatively low efficiency as an inhibitor while the residue, which gave a definite test for sulfur, had a high efficiency.

Instead of heating the sulfate, the same result may be obtained by heating the hydrochloride.

Example 5.—17.4 parts of a crude amine produced from kerosene and containing 25% of water were neutralized with 4 parts of 66° sulfuric acid containing 0.1% sulfur dioxide. The resulting product, which contained a small amount of an amine-sulfur dioxide reaction, showed a high efficiency as an inhibitor.

While in the foregoing examples, products derived from amines from kerosene with sulfur, sulfur dioxide and hydrogen sulfide have been described, it is to be understood the various amines described above may be combined with other low valence sulfur compounds, sulfur or polysulfides to give other amine-sulfur products which have high efficiency as pickling inhibitors, and that while in general the best results are obtained when a substantial proportion of sulfur or sulfur compound is combined with the amine, for example, when there is combined about one atom of sulfur for each molecule of amine, much smaller proportions of the sulfur or sulfur compound, down to mere traces, give effective results. The use of larger amounts of sulfur or sulfur compound, even largely in excess of the quantity which will combine, leaving free sulfur or free sulfur compound, is unobjectionable.

I claim:

1. A pickling bath for metals including a pickling acid, and as an inhibitor, a small amount of a reaction product of an aminated chlorinated aliphatic hydrocarbon with sulfur in a valence state less than six.

2. A pickling bath for metals including a pickling acid, and as an inhibitor, a small amount of a reaction product of an aminated chlorinated kerosene with sulfur in a valence state less than six.

3. A pickling bath for metals including a pickling acid, and as an inhibitor, a small amount of a reaction product of an aminated chlorinated aliphatic hydrocarbon with sulfur.

4. A pickling bath for metals including a pickling acid, and as an inhibitor, a small amount of a reaction product of an aminated chlorinated aliphatic hydrocarbon with sulfur dioxide.

5. A pickling inhibitor for acid pickling baths for metals comprising a reaction product of an aminated chlorinated aliphatic hydrocarbon with sulfur in a valence state less than six.

6. A pickling inhibitor for acid pickling baths for metals comprising a reaction product of an aminated chlorinated kerosene with sulfur in a valence state less than six.

7. A pickling inhibitor for acid pickling baths for metals comprising a reaction product of an aminated chlorinated kerosene with sulfur.

8. A pickling inhibitor for acid pickling baths for metals comprising a reaction product of an aminated chlorinated kerosene with sulfur dioxide.

9. The process of pickling metals which comprises exposing the metal to an aqueous acid containing a small amount of reaction product of an aminated chlorinated aliphatic hydrocarbon with sulfur in a valence state less than 6.

10. The process of pickling metals which comprises exposing the metal to an aqueous acid containing a small amount of reaction product of an aminated chlorinated kerosene with sulfur in a valence state less than 6.

11. The process of pickling metals which comprises exposing the metal to an aqueous acid containing a small amount of reaction product of an aminated chlorinated aliphatic hydrocarbon with sulfur.

12. The process of pickling metals which comprises exposing the metal to an aqueous acid containing a small amount of reaction product of an aminated chlorinated aliphatic hydrocarbon with sulfur dioxide.

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