Patented Aug. 12, 1930

1,773,024

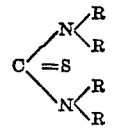
# UNITED STATES PATENT OFFICE

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## PROCESS FOR THE PICKLING OF METALS

No Drawing. Application filed April 12, 1929, Serial No. 354,696, and in Great Britain April 14, 1928.

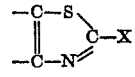
It is known that thioureas and substitution products of the type



in which R represents hydrogen, alkyl, aralkyl or aryl radicles act as inhibitors against the dissolution of metallic iron in pickling and similar processes. This however is an empirically ascertained fact, and, in the present state of knowledge, it is impossible to state the cause of this inhibitory effect or to predict what bodies will and what will not be effective inhibitors in the pickling process. By effective inhibitor we understand a body which while not retarding the cleansing action of the metal surface, i. e. the removal of metallic oxide or rust by acid, prevents or greatly hinders attack of the metal itself. It is also known that organic compounds containing a mercapto group are effective inhibitors in processes for the pickling of metal. This is disclosed in the British Patent No. 298,390 and the U. S. patent to Chamberlain No. 1,671,627. In the Chamberlain patent there is disclosed under the broad class of mercapto compounds the species of compounds known as mercapto thiazoles.

We have discovered that this inhibiting function is not confined to the mercapto thiazoles but the general class of bodies known as thiazole derivatives are very excellent inhibitors against attack of metallic iron or steel by acids and consequently of great value as additions to pickling and similar acid of cleansing baths.

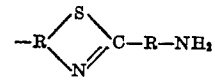
By thiazole derivatives we mean those bodies containing the following structural arrangement:



wherein X represents hydrogen, a group or radicle of simple or complex structure such for instance as $-CH_3$, $-C_6H_5$, $-SH$,



$-RNH_2$ or the following group



wherein the R of the radicles given above represents a phenyl residue which may or may not be further substituted with alkyl groups.

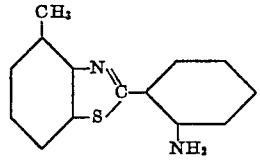
This inhibiting action is shown particularly by dehydrothiotoluidine bodies by which we understand the dehydrothiotoluidines proper, their ring substituted alkyl derivatives such as may be obtained for instance from xylidines containing a free ortho position adjacent to the amino group and the corresponding and closely related primuline bases. These dehydrothiotoluidine bodies may be obtained by the interaction of sulphur and toluidine or xylidine and like compounds as hereinafter more fully set forth. In the Chamberlain patent mentioned above there is specifically disclosed mercapto benzthiazole used as an inhibitor, but we have now found that this useful property appears to be possessed by thiazoles, benzthiazoles, naphthathiazoles and anthrathiazoles in general. As an example of typical inhibiting action exercised by dehydrothio-p-toluidine or the corresponding primuline base we mention that if 0.2 per cent by weight (reckoned on the weight of dilute acid used) of either of these substances be added to 25 per cent sulphuric acid (for cold pickling) or 5 per cent sulphuric acid (for hot pickling), the acid is found not to attack the metal to any appreciable extent during pickling, whilst without the addition the metal is etched very considerably.

We have found that the product from the interaction of sulphur and o-toluidine under conditions similar to those obtaining in the manufacture of dehydrothio-p-toluidine or primuline can be converted into a form suitable for use as an inhibitor by simple solution in 70 per cent sulphuric acid.

For example, we may heat together 7 parts of o-toluidine and 2 parts of sulphur for 6 hours at 185° C. and then for 18 hours at 210–215° C. Excess of o-toluidine is removed by distillation, preferably in steam or

under reduced pressure. The tarry product, from which water is decanted if necessary, is dissolved in 9 times its weight of 70 per cent sulphuric acid, or in suitable quantities of acid of other strengths. The solution so obtained is added in small proportion to the pickling acid: e. g., 1 lb. of the solution is sufficient for 4000 lbs. of 15 per cent hydrochloric pickling acid. This proportion may be varied to suit special conditions.

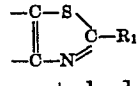
The compositions of the body obtained as above described from o-toluidine may be represented by the conventional formula for dehydrothio-o-toluidine.



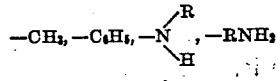
but it also contains more highly sulphurized bodies of the primuline type, the formula for which is not definitely known.

p-toluidine or suitable xylidines, i. e. such as contain a free ortho-position adjacent to the amino group, may be used in place of o-toluidine.

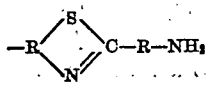
If it is preferred to use an isolated thiazole derivative instead of a solution in sulphuric acid, it may be diluted with salts such as sodium sulphate. We have discovered that the inhibiting function is possessed by a general class of compounds containing a certain structural arrangement, this structural arrangement being different from that of the general classes of compounds heretofore known as inhibitors. In the Chamberlain patent hereinbefore mentioned the inhibiting action was attributed to the presence of the mercapto group and it was not known that the thiazole grouping of certain specific compounds classified under the broad class of mercapto compounds was involved in the inhibiting action. We have found that compounds possessing the thiazole structure function as inhibitors irrespective of whether or not the mercapto group is present. In this application we claim the compounds possessing this inhibiting action which heretofore have not been utilized in processes of pickling of metals; that is thiazole derivatives containing the following general structural arrangement



wherein $R_1$ represents hydrogen,



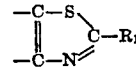
or the following grouping



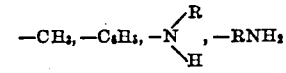
wherein R represents a phenyl residue which may or may not be further substituted with alkyl groups. The present invention is more particularly directed to certain compounds under this general class, namely, the dehydrothiotoluidine bodies.

What we claim and desire to secure by Letters Patent is:

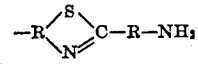
1. In a process of pickling metal, the step which comprises adding to the pickling acid bath an inhibitor to diminish the attack of the acid upon the metal without hindering the removal of scale or dust, the said inhibitor being a thiazole derivative containing the following structural arrangement



wherein $R_1$ represents hydrogen,



or the following grouping



wherein R represents a phenyl residue which may be further substituted with alkyl groups.

2. A process according to claim 1 in which the thiazole derivative used is a dehydrothiotoluidine body.

3. A process according to claim 1 in which the thiazole derivative used is dehydrothiotoluidine.

4. In a process of pickling metals, the step which comprises adding to the pickling acid bath a solution of a dehydrothiotoluidine body in sulphuric acid.

5. In an inhibitor for metal pickling baths, a new composition of matter comprising a strong aqueous solution of sulphuric acid and the reaction products of sulphur and orthotoluidine dissolved in said strong solution.

In testimony whereof we affix our signatures.

ERNEST CHAPMAN.
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