

## UNITED STATES PATENT OFFICE.

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## PROCESS OF DESULFURIZING OILS OR DISTILLATES.

SPECIFICATION forming part of Letters Patent No. 747,347, dated December 22, 1903.

Application filed February 25, 1903. Serial No. 145,072. (No specimens.)

*To all whom it may concern:*

Be it known that I, OTTO P. AMEND, a citizen of the United States, residing at New York, in the county of New York and State of New York, have invented new and useful Improvements in Processes of Desulfurizing Oils or Distillates, of which the following is a specification.

My invention especially relates to the elimination of sulfur from all hydrocarbon sulfur-bearing oils and distillates, at least from such sulfur-oils and the sulfur distillates obtained from oils found in Ohio, Indiana, Texas, California, and Canada. Hitherto many attempts have been made to obtain a simple, cheap, and effective process for the purpose. In some cases the desulfurization of the distillate has preceded the general acid treatment for refining, while in others it has been carried on simultaneously with it. The oxids and hydrates of some of the metals and alkalies have been used for the purpose. Some of these have been used with an application of heat and some with an absence of applied heat.

I desulfurize all of the above-described oils and distillates without heat as an aid to desulfurization.

I have found that in the presence of neutral saline solutions hydrate of copper will readily combine with sulfur of the sulfur compounds in the oils and distillates referred to, forming hydrosulfid of copper, which precipitates and which may be easily separated from the oil or distillate so treated. After such separation it can be shown that the oil or distillate is practically free of sulfur by testing the same with plumbate of soda, mercury, or with any of the well-known means employed to indicate sulfur reaction in oils. For the purpose specified I have found copper hydrates made from an aqueous solution of a soluble salt of copper the cheapest and most available.

In carrying out my invention I proceed as follows: I first wash the oil or distillate and blow it well with air, steam, or with both to

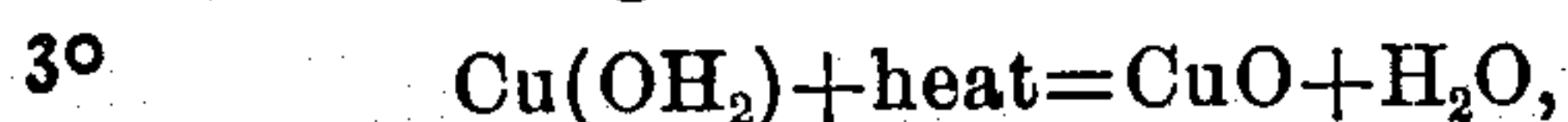
remove as much sulfureted hydrogen as possible, then remove the wash-water and add enough caustic solution (preferably caustic-soda solution, as it is the cheapest) to neutralize the organic acids found in the distillate, as may be shown by the use of litmus-paper. I usually employ of the caustic solution about one per cent. of the weight of the oil, the solution containing from three to five per cent. of caustic soda. After thorough agitation the caustic soda is drawn off. I then apply an aqueous solution of a soluble salt of copper (as sulfate of copper) in quantity about five per cent. of the weight of the oil or distillate and preferably one of 25° Baumé strength. After agitating the distillate and copper solution I add thereto of caustic soda or potash solution of 25° Baumé strength one-half of one per cent. of the weight of the distillate. The addition of this caustic solution gives a freshly-precipitated hydrate of copper, and at the same time which effects, with an excess of copper present, a neutral saline solution. The hydrated copper combines with the sulfur of the distillate, forming hydrosulfid of copper, and this, together with the surplus copper sulfate and the saline solution, settles to the bottom of the oil or distillate and is removed. After such removal the oil or distillate is thoroughly washed with water, and when well settled it may be subjected to the action of sulfuric acid to remove any copper or copper combinations that may be held in a state of suspension. After the removal of the sludge the oil or distillate is again thoroughly washed and for further refinement may be subjected to the usual acid and alkali treatment. It will be observed that the quantity of saline-copper solution used is largely in excess of the quantity of caustic and that while the quantity of caustic employed is sufficient to neutralize any acid introduced with the copper sulfate and to effect a partial precipitation of the copper there remains an excess of neutral saline-copper solution. Therefore the action of the caustic



must be to first neutralize the acid present, if there is any, and then with the remaining alkali to effect a partial precipitation of freshly-hydrated copper and the resulting sulfate of the alkali applied, leaving behind, when the caustic is exhausted, an excess of copper in the saline solution, thereby of necessity producing a neutral saline solution of the sulfate of copper which in consequence of its specific gravity separates quickly, after agitation, from the oil or distillate.

I am fully aware that distillates have been treated with copper and copper salts with an excess of acid and an excess of alkali, but have found in both cases that the product obtained was so permeated with copper that it was impossible to remove it with any ordinary acid and alkali treatment, and the presence of copper in the oil in any appreciable quantity not only clogs the capillaries of the wick, but so coats the end of the wick exposed to the flame with a visible copper covering that it destroys the light. Oil so affected is absolutely of no value.

I am also aware that hydrated copper has been used in the presence of heat; but it is well known that hydrated copper plus heat produces an oxid of copper plus water, as the following formula will show:



and the heat reaction so combines the copper with the oil as to render it inseparable except by redistillation.

The use of hydrated copper in a neutral solution, as described in this application, makes it possible to desulfurize the distillate without combining copper with it, and what copper is taken up or held in suspension by the distillate can be readily eliminated by subjecting it to the action of sulfuric acid, a removal of the sludge, and a thorough washing with water, thereby avoiding the present necessity of redistillation and further complex treatment.

With the lighter products of the distillate and the burning-oil distillate the method previously described in this application is employed exclusively. The heavy oils or lubricating stock in which the presence of neither acid nor alkali is permissible when finished a different after treatment is applied to effect the removal of the excess of copper. In consequence thereof I have made simultaneously herewith an application for separate Letters Patent therefor as an auxiliary to this invention, which was filed February 25, 1903, Serial No. 145,073, under the heading "Processes for desulfurizing oils and distillates."

I do not confine myself to the use of concentrated solutions of sulfate of copper and alkali, as very dilute solutions of the reagents specified, if used in sufficient quantity, will satisfactorily desulfurize the distillates, the

all important part being the use of a quantity of the copper solution in excess of the alkali solution and sufficiently so to produce a neutral saline solution, as hereinbefore set forth. I prefer the concentrated solutions only for the reason that it is easier to separate and remove them.

Having described my invention, what I claim as new, and desire to secure by Letters Patent of the United States, is—

1. The process of desulfurizing oil or distillate which consists: in eliminating the sulfurated hydrogen contained therein; in neutralizing the fatty and organic acids contained therein by subjecting them to the action of an alkali and then drawing off or removing the excess or settled alkali; in exposing the sulfur and sulfur compounds in the oil or distillate to the action of a soluble salt of copper in the presence of an alkali, but with the copper solution in excess of the alkali thereby producing a hydrated copper in a neutral saline solution; in removing the excess of copper, the copper hydrosulfids and residuum and exposing the remaining copper and copper sulfids to the action of sulfuric acid; and in removing the acid and sludge, substantially as described.

2. The process of desulfurizing oil or distillate which consists in neutralizing the fatty or organic acids contained therein; in exposing the sulfur and sulfur compounds therein to the action of a soluble salt of copper in the presence of an alkali; in producing a hydrate of copper in the presence of a neutral saline solution; in removing the excess of copper, the copper hydrosulfids and residuum and subjecting the oil or distillate to the action of sulfuric acid and then removing the acid and sludge, all substantially as set forth.

3. The process of desulfurizing oil or distillate which consists: in neutralizing the fatty or organic acids contained therein; in exposing the sulfur and sulfur compounds in the oil or distillate to the action of hydrated copper in the presence of a neutral saline solution; in removing the excess of copper, the copper hydrosulfids and residuum and subjecting the oil or distillate to the action of an acid and then removing the acid and sludge, all substantially as set forth.

4. The process of desulfurizing oil or distillate which consists: in exposing the sulfur and sulfur compounds therein to the action of a hydrate of copper in the presence of a neutral saline solution; in removing the excess of copper, the copper hydrosulfids and residuum and subjecting the oil or distillate to the action of an acid and then removing the acid and sludge, substantially as set forth.

5. The process of desulfurizing oil or distillate which consists: in exposing the sulfur and sulfur compounds therein to the action of copper hydrate in the presence of a neu-

tral saline solution; in removing the excess of copper, the copper hydrosulfids and residuum substantially as described.

5 6. The process of desulfurizing oil or distillate which consists: in exposing the same to the action of an alkali and to the action of a saline copper solution which is sufficiently in excess of the alkali to effect a neutral saline

solution; in separating the oil or distillate from the said chemicals and residuum and to washing with water substantially as described.

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Witnesses:

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