H. V. WALKER.

PROCESS OF DESULFURIZING PETROLEUM DISTILLATES.

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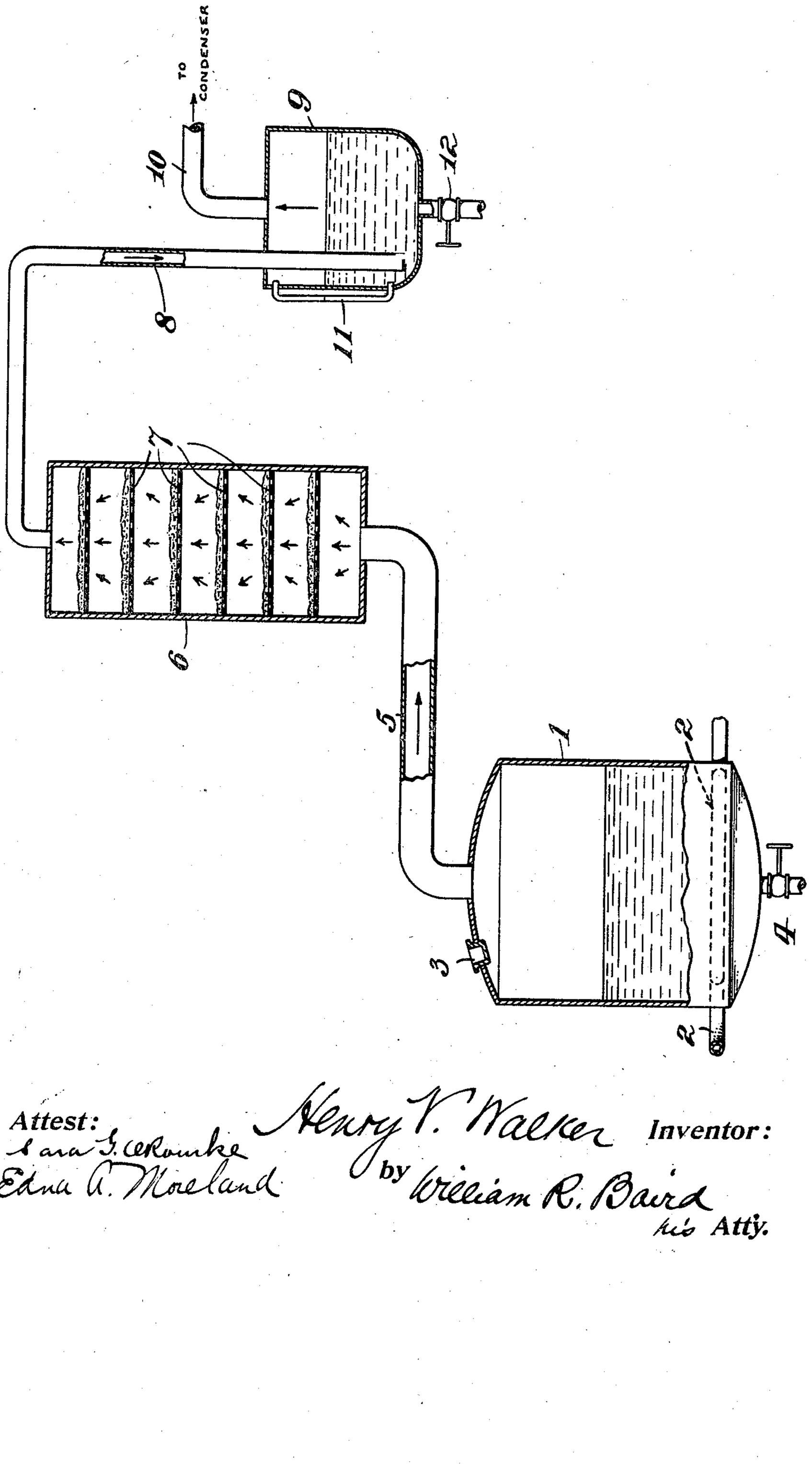
955,372. **Patented Apr. 19, 1910.**



Attest:
Sara J. McRourke
Edna A. Moreland

Henry V. Walker Inventor:
by William R. Baird
his Atty.

UNITED STATES PATENT OFFICE.

HENRY V. WALKER, OF BROOKLYN, NEW YORK, ASSIGNOR TO THE MAAS & WALDSTEIN COMPANY, OF NEWARK, NEW JERSEY, A CORPORATION OF NEW JERSEY.

PROCESS OF DESULFURIZING PETROLEUM DISTILLATES.

955,372.

Specification of Letters Patent. **Patented Apr. 19, 1910.**

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To all whom it may concern:

Be it known that I, HENRY V. WALKER, a citizen of the United States, and resident of Brooklyn, in the county of Kings and State of New York, have invented certain new and useful Improvements in the Process of Desulfurizing Petroleum Distillates, of which the following is a specification.

This invention relates to a process of desulfurizing petroleum distillates for the purpose of removing therefrom the sulfur compounds which impart to them an offensive odor by reason of which they are rendered unfit for many uses. This offensive odor is particularly characteristic of the oils of the Lima class and is due to the presence of sulfur in organic combination which cannot be removed by ordinary methods of refining, but which passes over into the condenser from the still with the vapors of the petroleum distillates.

Many attempts have been made to remove the sulfur from these oils and the most successful of them known to me depends on the use of oxid of copper. But this process is not completely successful and has other disadvantages not necessary to state here.

I have discovered that the desulfurization of these oils may be better and more readily accomplished by the use of anhydrous chlorid of copper and the best method known to me for carrying out this process is as follows: I take a suitable quantity of the ordinary crystallized chlorid of copper and heat it until all of the water, including the water of crystallization, is driven off, when it presents the appearance of a soft brown or red powder. The petroleum distillates may be subjected to the action of this anhydrous chlorid of copper by adding a small quantity of the powder to the oil, agitating the mass of the oil to produce thorough contact, removing the oil and washing it with water and distilling off the petroleum distillates, if necessary. This process is applicable to the treatment of oils which have been already distilled and condensed. I prefer, however, to carry out the process when the petroleum distillates are in the form of vapor. The vapors produced in any stage of the distillation process may be employed and a convenient and efficient way of subjecting the vapors to the action of the anhydrous chlorid of copper is to pass them through an apparatus in the form of a column containing the chlorid of copper in the form of a powder on a number of shelves with which the vapors must come in contact as they pass through the column. If it is found that the vapors passing out of this kind of an apparatus while free from offensive odors still contains a small amount of sulfur in the form of sulfureted hydrogen, it may be removed by passing such vapors through an alkaline lead solution. This is the ordinary plumbate of soda solution made by dissolving oxid of lead in a solution of caustic soda. It will be understood, of course, that the treatment of the vapors described takes place at a temperature high enough to maintain them in the form of vapor and that after the reaction has taken place they are condensed and collected in a suitable vessel.

In the annexed drawing is shown diagrammatically an apparatus in which the described process may be carried out.

1 is the still to contain the petroleum distillate to be treated, said still being heated in any suitable manner as by the live steam coil 2. The still may be filled through the inlet 3 and emptied at the valve controlled opening 4. A pipe 5 leads the vapors to the apparatus 6 containing perforated shelves 7 upon which is supported the anhydrous copper chlorid. The petroleum vapors, having passed through these perforated shelves and the copper chlorid, and being thus purified, are delivered by pipe 8 down below the surface of an alkaline lead solution or its equivalent contained in vessel 9, whence the final vapors escape by pipe 10 leading to a condenser not shown. A gage glass 11 is shown on the tank 9, also a valve controlled outlet 12. This tank will also naturally be provided with filling inlet, not shown however in the drawing.

This process yields a fluid entirely free from the offensive odor of the original and as colorless and limpid as water and one which will stand the tests usually applied to such substances.

In the process described the chlorid of copper is gradually converted into sulfid of copper. After such conversion it may be reconverted by roasting it in a suitable apparatus to convert it to an oxid and then treating it with hydrochloric acid to reconvert it into chlorid of copper which is dehydrated in the manner as above described,

when it may be used over again. The amount of chlorid of copper to be employed depends, of course, upon the amount of sulfur in the oil to be treated and in any particular case the proportion should be determined by previous experiment and calculation. When gas naphtha has been the material treated I have found that about two parts by weight of the anhydrous chlorid of copper to one hundred parts by weight of the gas naphtha is a suitable proportion.

Anhydrous copper chlorid dissolves in and seemingly forms a double compound with the sulfur bearing oil, which compound thereafter splits up into sulfid of copper, hydrochloric acid, and the sulfur-free oil. This is not true of copper sulfate which, whether anhydrous or not, is not taken up by the oil, forms no double compound, and is practically without effect in removing organically combined sulfur.

The alkaline lead solution as used above is not for the purpose of desulfurizing the oil, as this is completely effected by the anhydrous copper chlorid treatment. On the contrary, its purpose is to remove the small amount of sulfureted hydrogen produced by the action of the liberated hydrochloric acid upon the liberated copper sulfid. Similarly, the lead solution takes up said hydrochloric acid.

What I claim as new is:—

1. The process of desulfurizing petroleum distillates which consists first, in dehydrating chlorid of copper to remove the water of crystallization, and second, passing the petroleum distillates in the form of vapor over the anhydrous chlorid of copper thus formed and condensing the vapors.

2. The process of desulfurizing petroleum distillates which consists first, in dehydrating chlorid of copper to remove the water of crystallization, second, passing the petroleum distillates in the form of vapor over the anhydrous chlorid of copper thus formed and through an alkaline lead solution, and third condensing the purified vapors.

3. The process of treating gas naphtha and similar hydrocarbon compounds for the removal of sulfur present in organic combination which consists in subjecting the same to the action of anhydrous chlorid of copper.

4. The process of treating gas naphtha and similar hydrocarbon compounds for the removal of sulfur present in organic combination which consists in subjecting the same to the action of anhydrous chlorid of copper, in the proportion of two parts by weight of the latter and one hundred parts by weight of the former.

5. The process of treating petroleum compounds containing sulfur which consists in passing the same in the form of vapor over anhydrous chlorid of copper and through an alkaline lead solution.

6. As a step in the process of manufacturing petroleum distillates, the subjection of the same, or their vapors of distillation before condensation, to the action of anhydrous chlorid of copper.

Witness my hand this fourth day of February 1909, at New York, N. Y.

HENRY V. WALKER.

Witnesses:
WILLIAM R. BAIRD,
STEPHEN S. NEWTON.