

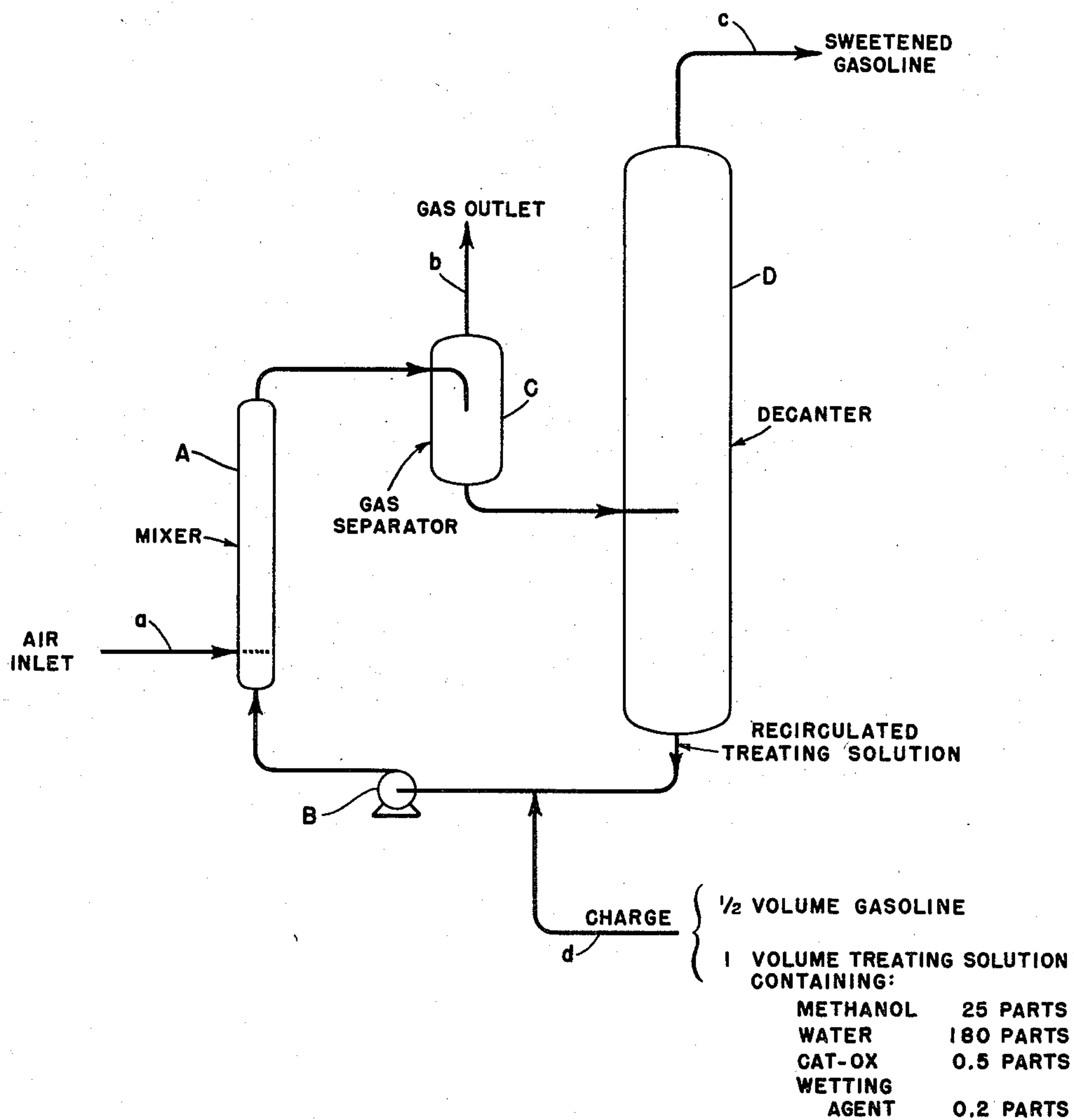
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PROCESS FOR REFINING PETROLEUM PRODUCTS

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PROCESS FOR REFINING PETROLEUM PRODUCTS

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19 Claims. (Cl. 196—29)

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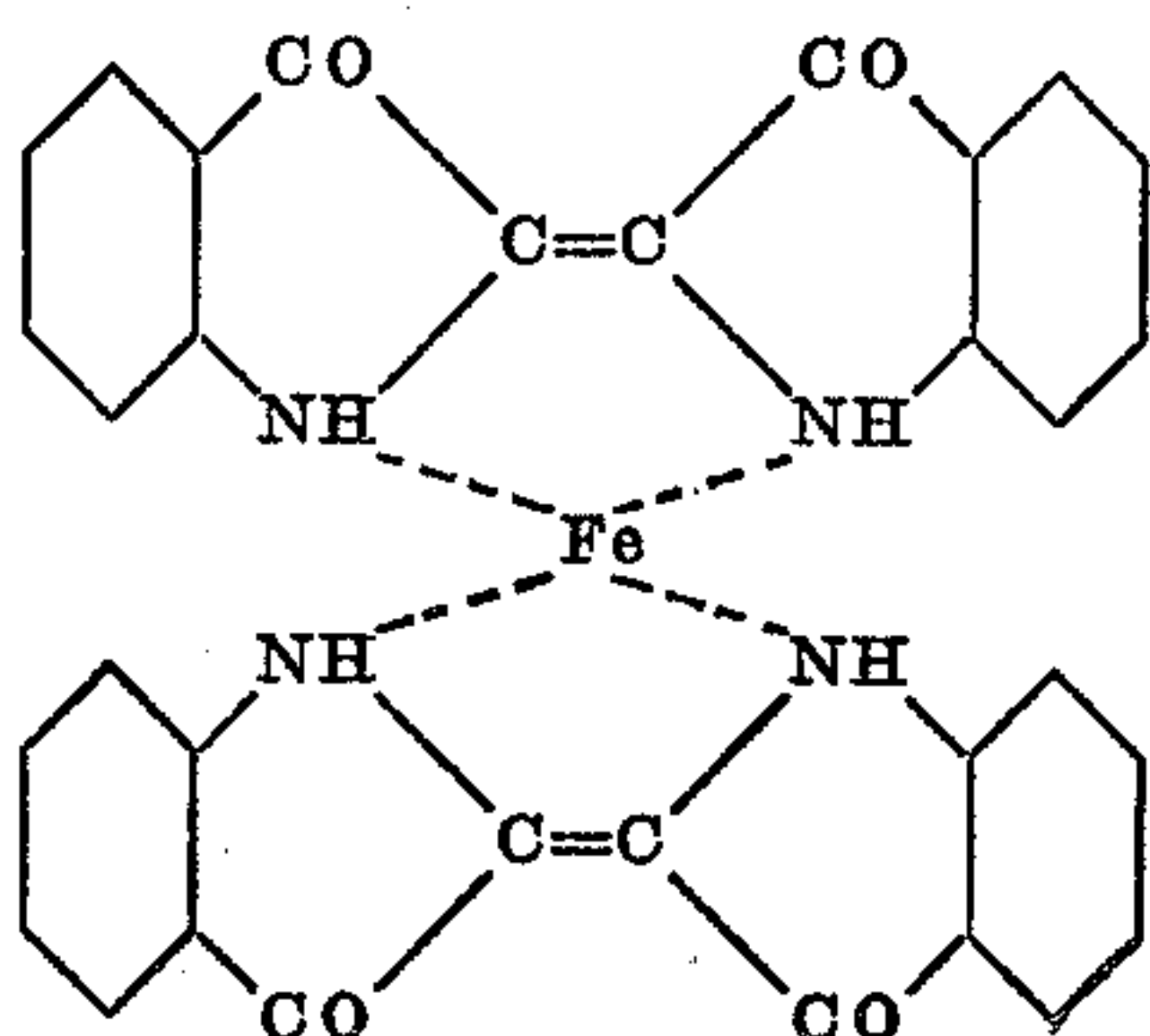
It is known that the mercaptans in petroleum products, and in particular in light products such as gasolines, naphthas, solvents, kerosenes, are eliminated by means of a refining operation which is generally known by the name of "sweetening" and which consists in converting the mercaptans into disulfides by oxidation. The usual process for effecting this refining is the plumbite process which comprises treating the petroleum products in question with a solution of alkaline plumbite in the presence of sulfur, the successive reactions being: formation of lead mercaptides, oxidation of same by means of sulfur with formation of organic disulfides and lead sulfide, and finally regeneration of the plumbite solution through oxidation by air of the lead sulfide in an alkaline medium.

The recognized drawbacks of this process are also known: since lead mercaptide is soluble in hydrocarbons, the lead sulfide is formed in the colloidal state in said hydrocarbons; since the decantation is slow, in order to accelerate it, it is necessary to add an excess of sulfur and this excess may be detrimental as regards corrosion, the octane number and susceptibility to lead. Furthermore, the exact quantity of sulfur to be used is often difficult to ascertain and the regeneration of the plumbite is a slow and comparatively costly operation.

Other processes, in which the oxidation is effected by means of metallic salts such as copper salts, also have serious drawbacks owing to the solubility of the metallic salt in the hydrocarbons treated.

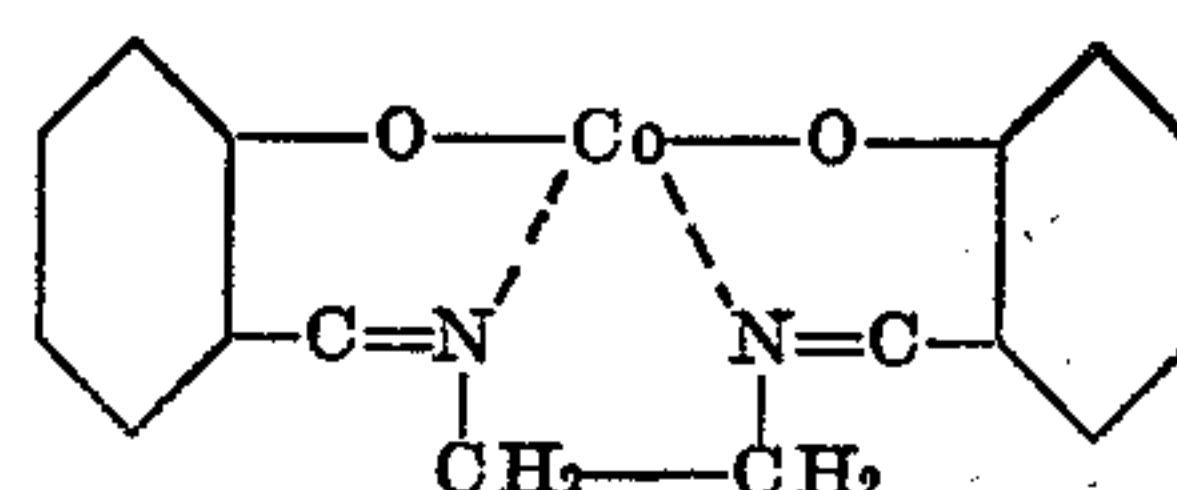
Endeavours have been made in various manners to effect the oxidation of the mercaptans by means of air, but heretofore no simple process has been discovered.

We have noted that certain organic substances and more especially organometallic compounds with chelated bonds, have the property of absorbing oxygen from air and of releasing it under certain conditions; such products include hemoglobin amongst the natural products, and also, amongst the synthetic products, the iron-indigo complex

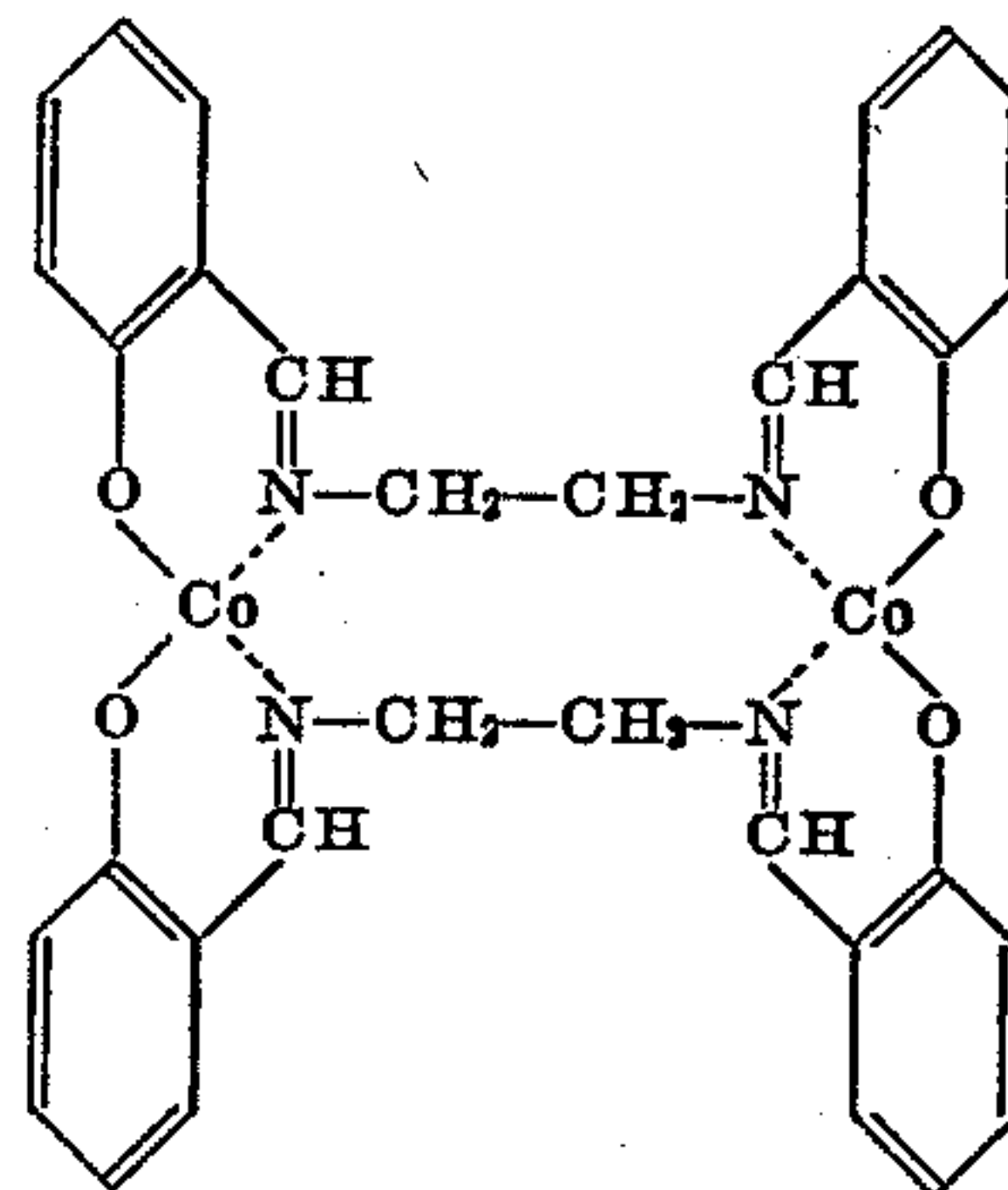


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disalicylal ethylene diamino cobalt



or bi-disalicylal ethylene diamine-aquo dicobalt



In a general manner, these compounds, some of which have now become industrial, absorb the oxygen from air at ordinary temperature and/or under pressure and release it in the pure state, either by increase of temperature, or in vacuo.

We have however observed this unexpected fact, viz. that in the presence of reducing agents, and in particular of mercaptans, the absorption and the exchange of oxygen are effected at the same temperature. The organic compounds in question behave in this case like real oxidation catalysts and the invention essentially lies in the novel application of said compounds to the elimination of the mercaptans contained in petroleum products.

In order to simplify the terminology, the compounds in question are hereinafter designated by the word "cat-ox" which is an abbreviation of "oxidation catalyst."

Thus, if 1 litre of gasoline containing 0.02% of sulfur in the form of mercaptans is shaken in air in the presence of 1 gram of cat-ox (bi-disalicylal ethylene diamine-aquo dicobalt, for example) it is found that, after 15, 30, 45 minutes, the proportion of mercaptans is successively 0.003, 0.005, 0.003 per cent. The gasoline can then be separated, the same quantity of gasoline containing mercaptans added, and the operation repeated. It is again found that there is a gradual oxidation of the mercaptans, and this takes place several times consecutively. This experiment clearly shows the catalytic effect of the cat-ox since it is well known that if gasoline containing mercaptans is merely shaken in air, such a result is not obtained.

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However, in this method of operation, the reaction speed is very slow and would not allow of the process being worked industrially.

We have furthermore observed that this reaction speed is considerably increased if certain organic compounds which are solvents for cat-ox are added to the hydrocarbon; amongst such compounds mention may be made, without this list being limitative, of methyl alcohol, ethyl alcohol, isopropyl alcohol, butyl alcohol and the like, ketones, dioxane, pyridine, and the like.

Thus, if the foregoing test is repeated by treating 1 litre of gasoline containing 0.02% of sulfur in the form of mercaptans with air in the presence of 1 gram of cat-ox, after adding 1 cubic centimeter of methanol, it is found that in five minutes the oxidation of the mercaptans is complete.

The same effect is obtained in the presence of water, that is to say if an emulsion of hydrocarbon containing mercaptans to be oxidized and a solution or a dispersion of cat-ox in a mixture of alcohol and water, acetone and water, pyridine and water, or the like, is treated with air.

From an industrial standpoint this modification of the invention has numerous advantages:

(a) The solvent is not lost in the hydrocarbon phase;

(b) No catalyst is lost by being carried away in the hydrocarbon;

(c) The quick decantation of the aqueous phase carries away the cat-ox in the hydro-organic medium and makes it possible to avoid any filtration of the hydrocarbon;

(d) It is possible to operate without a solid dispersion by using the solution of the catalyst in the hydro-organic medium chosen.

Various non-limitative examples of applications of the invention according to this modification are given hereinafter:

Example 1

A solution of 0.500 g. of cat-ox in 20 cubic centimeters of methanol and 180 cubic centimeters of water is prepared. The quantity of active oxygen in this solution is 25 mg. and can oxidize 100 mg. of sulfur in the form of mercaptan. 200 cubic centimeters of this mixture are shaken in the presence of air with 250 cubic centimeters of heptane containing 281 mg. of butyl-mercaptan. After 15 minutes allow to decant; separate the layer of heptane which does not contain any more mercaptan (Doctor test negative). Add the same quantity of heptane and mercaptan to the hydro-alcoholic phase; the mixture is "sweet" again after 15 minutes. The operation can be repeated 30 times without the activity of the hydro-alcoholic solution of cat-ox being decreased.

Example 2

240 cubic centimeters of the same hydro-alcoholic solution of cat-ox were used for treating as in the previous example 250 cubic centimeters of Irak distilled gasoline containing 0.0336% of sulfur in the form of mercaptans. After 25 minutes the gasoline was sweet. The gasoline was separated and the same quantity of gasoline treated again. The operation was repeated 25 times without observing any decrease in the catalytic properties.

We have furthermore found that the speed of reaction is increased if the contact between the phases is improved by adding a surface-active or wetting agent as is apparent in the next example.

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Example 3

If 250 cubic centimeters of gasoline containing 82 mg. of sulfur in the form of mercaptans are treated in air with 200 cubic centimeters of a hydro-alcoholic solution containing 0.423 g. of cat-ox, the gasoline becomes sweet after 25 minutes. The same test was repeated, adding 1 per mil of sodium isopropyl-naphthalene-sulfonate to the aqueous phase; the oxidation of the mercaptans was completed in 10 minutes.

The addition of any other surface-active or wetting agent, and in particular a sodium sulfonate, produced similar results.

Furthermore, it was observed that the addition of such a surface-active or wetting agent favors the breaking up of the gasoline-aqueous solution emulsion and accelerates the separation of the phases.

The speed of reaction is proportional to the ratio between the quantity of catalytic oxidation agent and the quantity of mercaptan to be oxidized, as shown by the following example:

Example 4

65 cubic centimeters of gasoline containing 15 mg. of sulfur in the form of mercaptans are treated in air with 220 cubic centimeters of a hydro-acetone solution containing 1.6 per mil of cat-ox containing 5% of active oxygen and 1 per mil of sulfonate. Sweetening is obtained in 15 minutes.

If only 30 cubic centimeters of gasoline are treated with the same volume of the same solution, sweetening is obtained in 3 minutes.

Example 5

The reaction can be carried out in a continuous manner, and by way of example the following apparatus and process are described with reference to the accompanying drawing.

1 volume of a solution comprising 25 parts by weight of methanol, 180 parts of water, 0.5 part of bi-disalicylal ethylene diamine aquo-cobalt, 0.2 part of sodium butylnaphthalene sulfonate and $\frac{1}{2}$ a volume of gasoline to be refined, are discharged per unit of time into a static mixer A by means of a pump B. A quantity of air that corresponds at least to the quantity of sulfur to be oxidized is blown in at the bottom of the mixer. After passing through a gas remover C in which the excess of air is separated at b, the emulsion of the liquid phases is conveyed to a decantation tower D, at the top of which the sweet gasoline is continuously removed at c; at the bottom of the tower the hydro-alcoholic phase containing the catalyst is exhausted by the pump B and discharged into the mixer after adding the gasoline to be treated which is admitted at d.

By way of a modification, it is possible to use an excess of cat-ox dispersed in the hydro-alcoholic phase, so that the same is constantly saturated; it is also possible to cause the gasoline-methanol-water emulsion to flow towards a solid mass of cat-ox while air is being blown; all these techniques also produce the sweetening of the gasoline treated.

What we claim is:

1. A process for refining petroleum products, which comprises effecting the oxidation of the mercaptans contained in said products by the action of oxygen in the presence of organic-chelate compounds that have the property of absorbing oxygen from air and of releasing it in a pure state, said chelate compounds having

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metallic constituents and said chelate compounds behaving in this case as oxidation catalysts.

2. Process according to claim 1, wherein the absorption and exchange of oxygen are effected without change of temperature or pressure.

3. Process according to claim 1, wherein the oxidation is effected in the presence of a third substance chosen among the solvents for the chelate compound which is used.

4. Process according to claim 1, wherein the oxidation is effected in the presence of an alcohol.

5. Process according to claim 1, wherein the oxidation is effected in the presence of a ketone.

6. Process according to claim 1, wherein the oxidation is effected in the presence of a solution of the compound used in a mixture of water and an organic solvent for said compound.

7. Process according to claim 1, wherein the oxidation is effected in the presence of a dispersion of the compound used in a mixture of water and an organic solvent for the said compound.

8. Process according to claim 1, wherein the oxidation is effected in the presence of a solution of the compound used in a mixture of water and an organic solvent for said compound and in the presence of a surface active compound.

9. Process according to claim 1, wherein the oxidation is effected in the presence of a dispersion of the compound used in a mixture of water and an organic solvent for said compound, and in the presence of a surface active compound.

10. Process according to claim 1, which is carried out in a continuous manner.

11. Process according to claim 1, which is carried out in a discontinuous manner.

12. Process according to claim 1, which is carried out at ordinary pressure.

13. Process according to claim 1, which is carried out at a pressure that differs from ordinary pressure.

14. The process of refining liquid petroleum products which comprises oxidizing mercaptans contained in said products by the action of oxygen in the presence of a catalyst which is comprised of cobalt and organic components which react to form a compound having a chelate bond.

15. The process of refining liquid petroleum products which comprises oxidizing mercaptans contained in said products by the action of oxygen in the presence of a catalyst which is comprised of disalicylal imino cobalt.

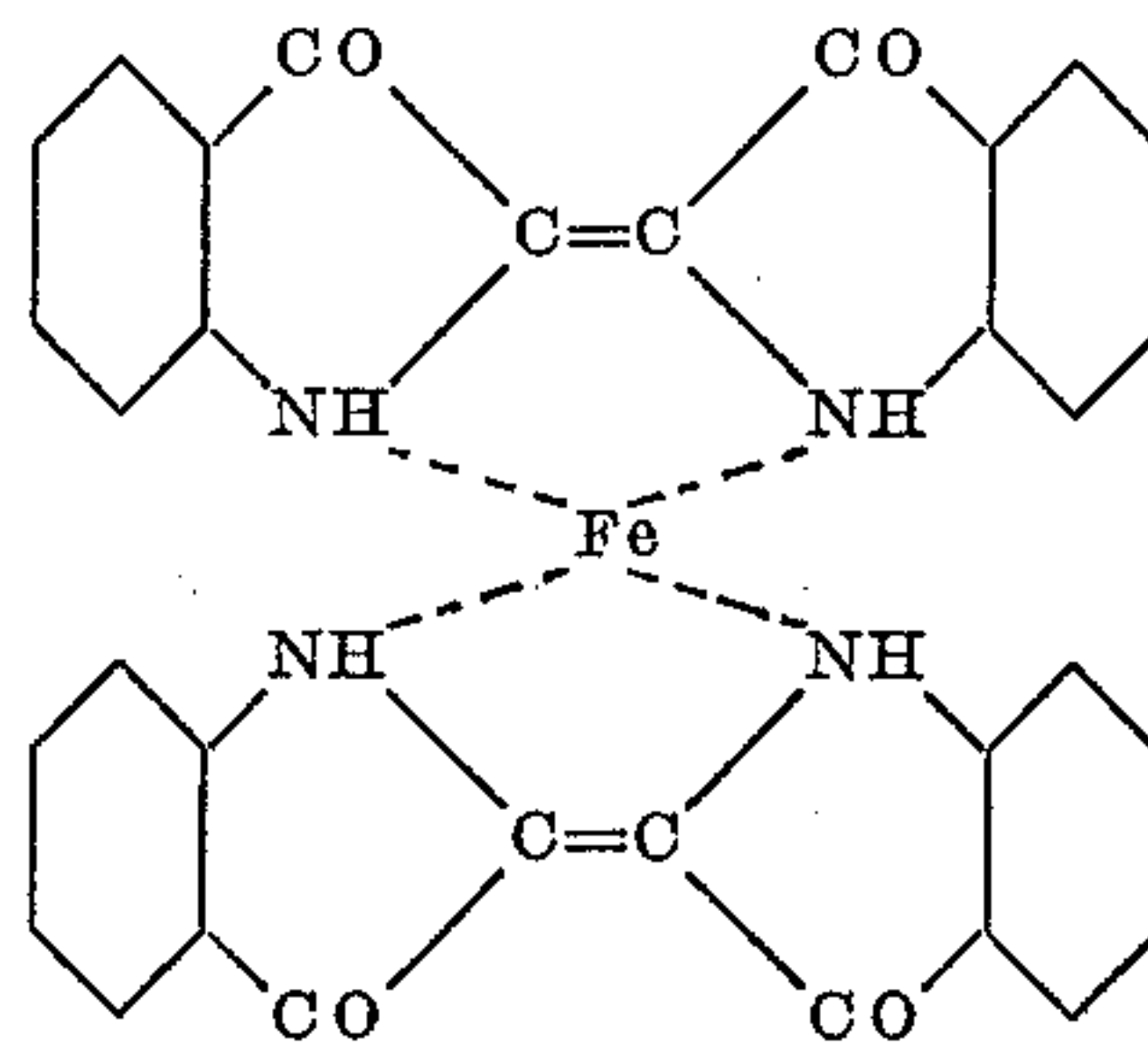
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16. The process of refining liquid petroleum products which comprises oxidizing mercaptans contained in said products by the action of oxygen in the presence of a catalyst which is comprised of iron and organic components which react to form a compound having a chelate bond.

17. The process of refining liquid petroleum products which comprises oxidizing mercaptans contained in said products by the action of oxygen in the presence of a catalyst which is comprised of disalicylal ethylene diamino cobalt.

18. The process of refining liquid petroleum products which comprises oxidizing mercaptans contained in said products by the action of oxygen in the presence of a catalyst which is comprised of bi-disalicylal ethylene diamine-aquo dicobalt.

19. The process of refining liquid petroleum products which comprises oxidizing mercaptans contained in said products by the action of oxygen in the presence of a catalyst which is comprised of the iron-indigo complex



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