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PROCESS FOR SWEETENING SOUR HYDROCARBON OILS

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This invention deals with the sweetening of sour hydrocarbon oils, and more particularly is concerned with an improvement of so-caled copper sweetening processes to produce sweetened hydrocarbon oils which are free from corrosive sulfur.

In the past, several sweetening processes have been developed in which mercaptans contained in sour hydrocarbon oils are oxidized to disulfides with the aid of molecular oxygen, e. g., air, and a copper catalyst. Suitable copper catalysts are, for example, metallic copper, various copper oxides and salts, and particularly cupric chloride and cupric sulfate. The catalyst may consist essentially of copper or copper compounds, or it may be used in conjunction with auxiliary catalysts such as active clays, or salts of other metals or of ammonia; or it may be simply deposited on a more or less inert suitable carrier. The reaction may be promoted by the presence of acid or basic gases as SO_2, HCl, NH_3, etc. Oxygen necessary for the oxidation is normally introduced during the sweetening process in the form of free oxygen or gas containing it, such as air; or else a cupric compound may be employed for effecting the oxidation reaction of the mercaptans to disulfides and the resulting cuprous compound is then separately regenerated to the cupric compound by a suitable oxidation process.

A difficulty which frequently arises in connection with copper sweetening is that the sweetened gasoline contains small amounts of corrosive sulfur. It has been suggested that this corrosive sulfur be removed by treatment with inorganic sulfides such as aqueous solutions of sodium sulfide, etc., according to the reaction:

$$Na_2S+S=Na_2S_2$$

However, in spite of thorough treatment with different sulfides and under wide range of conditions, traces of corrosive sulfur of the order of .0002–.0003 grams/100 cc. remain in the treated oil, which are sufficient to be of consequence, particularly in special solvents such as cleaners' naphthas, painters' solvents, etc. Many of the specifications for special solvents call for a negative corrosion by the so-called copper strip corrosion test in which a polished copper strip is placed in the flask during a standard A. S. T. M. distillation and allowed to remain until the end point of the distillation has been reached. The strip is then removed and observed for discoloration. The amount of sulfur liberated in copper sweetening process is normally sufficient to cause a tarnish under the conditions of this test which is not eliminated by treatment with a sulfide.

Now we have discovered that the harmful corrosive sulfur can be removed effectively by an exceedingly simple additional step. Our treating method consists of passing a major portion of the sour oil to be sweetened through a copper catalyst under conditions to effect the customary sweetening, and by-passing a remaining minor portion of pre-determined volume around the catalyst. The sweetened and unsweetened portions are then combined, and the resulting very slightly sour mixture is then washed with a sodium plumbite solution.

The ratio of the two portions, i. e., of the sour and the sweetened, is such that the amount of corrosive sulfur liberated in the copper sweetening approaches one-half of the amount of mercaptan sulfur contained in the unsweetened portion. In contact with the plumbite solution, the sulfur and the mercaptan react as follows:

$$2RSH+S+PbO=RSSR+PbS+H_2O$$

Inasmuch as the quantities of the free sulfur in copper-sweetened oils are quite small, it is difficult to determine them accurately by analytical methods, and therefore it is in general not practical to base a determination of the ratios of the two portions on analytical determinations. Instead, it is easier to determine suitable ratios by a series of simple laboratory tests in which copper-sweetened and unsweetened portions of the oil are combined in various ratios and the resulting several mixtures are washed with plumbite solution. All treated mixtures are then examined for corrosion as described earlier, as well as for sourness. If the ratio of unsweetened to sweetened portions is too high, the treated oil is sour; if it is too small, it is corrosive. Only over a relatively narrow range of ratios is the product both non-corrosive and doctor sweet. Any ratio within this range may be chosen as coming within the requirements stated above, i. e., that the amount of the free sulfur in the sweetened portion must approximate one-half of the mercaptan sulfur in the unsweetened portion.

The exact range of suitable ratios varies somewhat depending upon the oil, as well as on the conditions of the copper-sweetening step, because these variables control the amount of free sulfur found in the copper-sweetened oil. In general, however, suitable ratios of unsweetened to copper-sweetened oil lie between about 1:20–1:5.

The plumbite washing consists essentially of contacting the slightly sour mixture of sweetened and unsweetened oils with a solution of sodium plumbite. No sulfur is added, as would be the case in conventional doctor sweetening.

In the latter type of process, the consumption of chemicals is a function of the sourness, i. e., the concentration of mercaptans in the oil to be sweetened. In the combination process of this invention, the amount of chemicals consumed, other than oxygen or air required in the copper-sweetening step, is exceedingly small, because the mercaptan content of the mixture which is

plumbite-treated is only a small fraction, usually less than 20% of the original mercaptan content, and no additional sulfur is required to complete the reaction. For this reason, the combination process of this invention makes possible considerable savings over conventional doctor or plumbite sweetening.

The following example illustrates our invention:

A charge of sour VM and P naphtha was sweetened by passing it, together with air, through a tower containing a mechanical mixture of 25% copper sulfate, 25% ammonium chloride and 50% Attapulgas clay. Portions of the sweetened naphtha were then mixed with various percentages of the sour charge, and the resulting mixtures were washed with plumbite in the absence of added sulfur. The plumbite-washed naphthas were water-white and had a sweet odor. Results are tabulated below:

Material	Plumbite-washed	Doctor test	Copper-stripped corrosion test
Charge to tower (1)	No	Sour	Negative.
Copper sweetened (2)	No	Sweet	Slight tarnish.
Copper sweetened	Yes	do	Do.
4% (1)+96% (2)	Yes	do	Do.
6% (1)+94% (2)	Yes	do	Negative.
8% (1)+92% (2)	Yes	do	Do.

We claim as our invention:

1. In the process of sweetening sour hydrocarbon oil containing mercaptans by treatment with a copper catalyst whereby mercaptans are converted to disulfides, the improvement comprising passing a major portion of said sour oil through said catalyst to effect conversion of mercaptans to disulfides and to result in a sweet oil containing a small amount of corrosive sulfur, combining a pre-determined amount of the remaining portion of said sour oil with said sweetened oil, the ratio of the sweet and sour oil portions so combined being such that the content of corrosive sulfur in the sweet oil is approximately one-half of the mercaptan sulfur in said sour portion, and washing the resulting slightly sour mixture with an aqueous solution of sodium plumbite.

2. The process of claim 1, wherein said copper catalyst comprises cupric chloride.

3. The process of claim 1, wherein said copper catalyst comprises copper sulfate.

4. The process of claim 1, wherein the ratio of sour to sweetened portions in said mixture is 1:20–1:5.

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