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AMENDED SPECIFICATION

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PATENT SPECIFICATION

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3692

COMPLETE SPECIFICATION

Process for Desulphurising Gases

We, STUDIEN- UND VERWERTUNGS-GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG of Mülheim-Ruhr, Germany, a German Company, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

It is known that organic sulphur compounds can be removed from gases containing carbon monoxide and hydrogen by passing the gases over carbonates of the alkaline metals at a high temperature. In a process carried out in America particulars of which were published in this country prior to the date of this application carbon bisulphide was converted into hydrogen sulphide by passing coke oven gas containing it over a very active iron oxide at about 230° C.

It has been found that it is possible for the sulphur with the exception of thiophene to be substantially completely removed without there being left any trace of hydrogen sulphide, in the gas that is being removed, by treating the gases at temperatures lying between 150° C. and 300° C. with alkali metal carbonates which have been intimately mixed with reactive oxides or hydroxides of iron. It has been found that purifying compounds which consist of such mixtures are capable of removing substantially all the sulphur compounds with the exception of thiophene very effectively, so that if the work be carried out properly there is substantially no trace left of sulphur with the exception of thiophene, either in organic combination or as hydrogen sulphide. This reaction was neither known nor could it have been foreseen. The use of gas purifying compounds known as "alkalised" compounds which contain only a small percentage of alkali, in one instance a mixture of soda ash and sawdust and are intended merely for producing an alkaline reaction or for activating the hydrogen sulphide absorbed, does not fall within this invention. The reaction according to the invention is dependent upon the presence of large quantities of alkali metal carbonates amounting to at least 10%. The alkali metal carbonate cannot be replaced by carbonates of alkaline earths such as lime, as is the case, for example, when producing "alkalised" gas purifying compounds.

It has been found that intimate mixtures of 1 to 2 parts of soda with 2 to 3 parts of reactive oxides or hydroxides of iron are very effective. For this purpose suitable iron ores, such as bog iron ore, as also the residues from the treatment of bauxite, which are generally used as "dry" gas purifying compounds may, for example, be used. For producing the mixtures described it suffices to rub together very intimately in a dry state the two constituents alkali metal carbonate and iron oxide. This mixture may then be used in the form of powder or in the form of briquettes made from the powder.

It is, however, advantageous to bake this mixture after stirring it with water to produce a stiff paste, until a solid mass is produced; this is broken up into hard lumps, which retain their shape or mechanical compactness even at the reaction temperature, and notwithstanding this, they can be used effectively for the purifying operation by reason of the great porosity of the lumps. In order to be able to mould the composition more easily it is useful to add water glass solutions to the composition; furthermore the breaking-down of the composition can be assisted by the addition of porous substances such as kieselguhr.

The object of the process according to the invention is to desulphurise those gases which contain carbon monoxide in addition to hydrogen. It is known, however, that iron or iron compounds, particularly when in the presence of alkali, give rise to a catalytic effect in various ways with mixtures of carbon monoxide and hydrogen when at high temperatures. It has been found that notwithstnding this fact, it is possible according to the present invention substantially completely to desulphurise except for thiophene those gases which contain carbon monoxide in addition to hydrogen without undesirable subordinate reactions of the carbon monoxide occurring in the completely desulphurised gas. The mixtures of alkali metal carbonate and iron oxide produced by the method hereinbefore described exert a practically complete desulphurising action except for thiophene even at considerably lower temperatures than those at which, as experience has shown, the carbon monoxide is catalytically attacked in the same compounds. Accordingly in carrying out the purifying operation according to the present invention the reaction temperatures are maintained so low that substantially complete desulphurisation except for thiophene is obtained, and undesirable subordinate reactions do not occur.

According to a known process the desulphurisation of gases is effected by the use of alkaline substances or alternatively by the use of oxides and hydroxides of iron and zinc. Temperatures up to 500° C. however must be employed. When using the last mentioned substances with high temperatures destructive subordinate reactions occur when gases containing carbon monoxide are used, whereby the composition of the gas being purified immediately changes. When using the purifying compounds according to the invention, which likewise contain iron oxides and which in the use of considerably lower temperatures effect the substantially complete removal of all the sulphur compounds with the exception of thiophene, in which it differs from the known processes, these otherwise objectionable subordinate reactions of the gas constituents do not occur, so that during desulphurisation the composition of the gas treated is not materially changed.

With a view to the avoidance of undesirable subordinate reactions desulphurisation may be continued at a relatively low temperature, for example, at between 200° C. and 230° C., until the composition is exhausted. A considerable improvement in the efficiency of the purifying compositions is possible, however, by gradually raising the reaction temperature in the composition up to a maximum of 300° C., as the activity of the purifying mass with reference to the setting up of undesirable subordinate reactions decreases proportionately as the charging of the purifying masses with sulphur increases. If on the other hand such gradual increases in temperature are not possible a steady temperature higher than 230° may be employed from the outset.

If the purifying compositions after being used for a long period no longer produce a desulphurising action at the higher temperature, their capacity for absorbing sulphur is not completely exhausted. It has been found that exhausted purifying mixtures after being moistened with water can be still further used for the purpose of removing hydrogen sulphide from the raw gases in known manner at room temperature.

EXAMPLE.

Water gas containing no hydrogen sulphide or thiophene, but about 30 grammes of organically combined sulphur per 100 cubic metres is conveyed at 230° C. at a velocity of 500 chamber volumes of gas per hour through a reaction chamber over a purifying composition in small lumps, the composition being produced by the baking and breaking up of 1 part of soda and 2 parts of hydrated iron oxide (Luxmasse) or instead of the latter 2 parts of red sludge ("Rotschlamm"), that is to say, the residue from the decomposition of bauxite with alkali, which residue is rich in ferric oxide, and which is used in dry form in connection with the dry desulphurisation of gas. Under these conditions 1 kg. of the mixture purifies 100 cubic metres of gas so thoroughly that there is not indication when the gas is tested by any of the usual methods that any sulphur remains in any form in the gas, and without the composition of the water gas being changed.

If the reaction temperature is raised to 300° 1 kg. of the composition purifies as much as 350 cubic metres of gas.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

A process for removing the sulphur compounds (with the exception of thiophene) from gases containing carbon monoxide and hydrogen, characterised in that alkali metal carbonates are employed to the extent of at least 10% in intimate admixture with reactive oxides or hydroxides of iron at temperatures lying between 150° C. and 300° C., but maintained so low that the purifying mixture employed at no time produces subordinate reactions of carbon monoxide.

Dated this 21st day of January, 1935.

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Agents for the Applicants.

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