

of the product; this clearing may be carried as far as desired, depending on the amount of adsorbing agent used and on the other experimental conditions applied. Furthermore, this process leads to extensive removal of the iron contained in the products. This is very surprising because a large part of the iron is present in the form of organic compounds which are usually hard to remove or to clear.

As diluents, hydrocarbons of varying constitution may be considered, especially aliphatic and alicyclic ones; among the latter, methylcyclohexane, isopropyl cyclopentane and alkyl substituted decahydronaphthalene may be given as examples.

In general, completely saturated hydrocarbons are to be preferred to those of the same structure but containing one double bond. For instance, a hexane is preferable to a hexylene, a cyclohexane better than a cyclohexene. As diluents or solvents, individual compounds or mixtures may be used; among the latter are especially those products which are obtained on industrial scale, especially fuels prepared by high-pressure hydrogenation of brown coal tar, brown coal, coal, etc., or also the fuel fractions obtained by the reduction of carbon monoxide with hydrogen, such as for instance the so-called Kogasin I; and also other industrial products such as fuel obtained from the brown coal low temperature carbonization process\*, either in crude form or after a further treatment such as for instance hydrogenation.

As adsorbents, various large-surface substances may be used; as examples, we may cite: natural or artificial bleaching earths such as Fuller's earth, Floridine, Terrana, etc.; further-

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\*Schwelbenzin (Transl.)

more, other adsorbing substances such as active coal, solid gels of silicic acid, aluminum hydroxide and others. Mixtures of these adsorbents may also be used. Furthermore, if one operates in several stages, different adsorbents may be used for each stage, e.g. active charcoal in the first stage and a bleaching earth in the subsequent stage. The temperature applied for the clearing process can vary within wide limits. Liquid products may be purified at ordinary temperature. Others, which are of high viscosity or solid, and which only at higher temperatures have a sufficient solubility in the above mentioned hydrocarbons, may be treated at temperatures of 50°, 80°, 100° and higher.

The adsorption equilibrium will be reached more rapidly if the liquid containing the substances to be purified is continually agitated. If the adsorbing agent is in form of a powder, this can be accomplished by stirring; with solid adsorbents, the same effect can be reached by continually pouring the liquid over the chunks of adsorbent, e.g. by fixing the latter in a tower and then pumping the liquid over it.

The amount of solvent which contains hydrocarbon depends on its nature as well as on the composition of the solute, and furthermore on the temperature applied. In general, it may be within very wide limits; it may be smaller, equal to, or considerably greater than the substance to be cleared.

Similarly, the amount of adsorbent depends on the other conditions and may be varied within a wide range. In general, it amounts to only a fraction (e.g. from 1%-30%) of the weight of the total amount of substance to be cleared. The separation

of the adsorbing agent from the liquid may be carried out by any one of the known methods, such as filtration, sedimentation, centrifugation and similar procedures. The adsorbent may be freed from the liquid parts which stick to it, by thorough washing.

The procedure described is especially suitable for the breakdown of those synthesis products or of their higher boiling components, which contain, besides hydrocarbons, also a considerable amount of oxygenated organic compounds; especially alcohols and other products which are formed during the conversion of carbon monoxide with hydrogen in the presence of iron catalysts at medium pressures (ab. 8-25 atm.) and at temperatures below 250° which are definitely below the level at which mainly or exclusively hydrocarbons are formed. But also those synthesis products which consist mainly or exclusively of hydrocarbons, may be cleared by the procedure described above.

After use, the color of the adsorbent almost always ranges from dark brown to a deep black, and the adsorbent itself is no longer suitable for further use. It was found that the adsorbent may be regenerated by a very easy method which consists in treating it with organic, oxygenated, halogenated or cyclic solvents; this treatment may be followed by a further treatment with acids. By means of the solvent, the adsorbent is extensively cleared, should it have been of light color already before use as adsorbent. By treatment with acid, which may be carried out in aqueous, alcoholic or also other solution, the regeneration of the adsorber is still increased. For this purpose,

dilute hydrochloric acid, sulfuric acid or similar acids may be used. The adsorbent treated with acid is then centrifuged, thoroughly rinsed with water and treated, for the removal of the latter, with an organic solvent; thus after desiccation or removal of the last named solvent by the above-mentioned hydrocarbon-containing solvent, they may again be used as solvents.

The oxygen-containing solvents which may be considered for our purposes are: low alcohols, such as ethanol and propanol; esters, such as acetic acid ethyl esters or butyl acetate, propyl formate or other formic acid esters of the low molecular alcohols; ketones, such as acetone and methyl ethyl ketone, ethers, such as diethyl ether, dipropyl ether, dibutyl ether and others. These substances may be used individually or in mixtures. Examples of halogen-containing solvents are: chlorine compounds such as trichloro ethylene, chloroform, carbon tetrachloride and also the compounds of other halogens, such as dibromo propane. As cyclic compounds are of importance: decahydronaphthalene, tetrahydronaphthalene and, above all, the strongly unsaturated hydrocarbons such as benzene, toluene, xylene, etc. The treatment of the adsorbing agents with these solvents occurs as a rule at their boiling temperatures which, depending on whether higher or lower pressures are used, will be correspondingly lower or higher. The best operating temperature is between 50 and 150°. The period of the treatment, which depends on the nature of the substances which are to be adsorbed, amounts usually to two hours or more; in some cases, the treatment extends to 8-12 hours; on the other hand, it may also be less than two hours.

The clearing action described in the above paragraphs is sufficient for using the various products as waxes for the coating of linoleum, furniture, leather, etc., and for similar purposes. On the other hand, the products cannot be used as cream base\* since

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\* Salbenzusatz (Transl.)

the degree of clearing is not yet sufficient for pharmaceutical or cosmetic purposes. Furthermore, small amounts of unknown odorants are still present which have a disturbing effect.

It was now found that still further clearing may be achieved very advantageously by hydrogenation. This hydrogenation runs much better after the adsorptive process than without it. In the latter case, much sharper hydrogenation conditions must be maintained in order to achieve total discoloration; when this is the case, the high molecular compounds split partly into lower molecular compounds and even gaseous hydrocarbons are formed. If high boiling residues are hydrogenated without previous bleaching, a faintly grey-green color tone remains whereas pre-bleached products become white after hydrogenation. If alcohols, esters and similar compounds are contained in the products, these compounds, when subjected to hydrogenation, are converted to a great extent into hydrocarbons if they are not pre-bleached; this decreases the value of the reaction products greatly. If, however, one hydrogenates after the above-described adsorptive treatment, substantially milder conditions will suffice. One may thereby conserve the alcohols almost completely and, if one wishes, one may split the esters present in the product into alcohols; thus, not only the color of the product may be changed, but it may also be considerably improved in its chemical composition. Furthermore, the adsorptive pretreatment of the synthesis products greatly lengthens the life of the hydrogenation catalyst.

The hydrogenation is carried out, depending on the effectiveness of the particular catalyst employed, at temperatures

varying between 200 and 400°C.; in general, however, the temperature is much lower, e.g. by about 30°, than the temperature required for the hydrogenation without previous adsorptive treatment of the products. It will be advantageous to work at higher pressure, such as 50 atmosphere or, better, even higher; especially favorable is a 200 atm. pressure. The treatment can be made in individual batches or in one batch, in the autoclave; or continuously in a high pressure reactor with heatable in and outlets through which trickle the products to be subjected to the hydrogenation. The contact time of the products in the hydrogenation reactor, i.e. the period of hydrogenation in the continuous operation, amounts to anywhere between 1/2-2 hours; the rate of throughput per hour is 0.5-2 space units of product per catalyst space unit.

As hydrogenation catalysts, the various compounds known to be efficient may be used; for instance copper chromite, copper barium chromite, cobalt, nickel, copper and similar metals; furthermore some sulfur containing compounds such as molybdenum sulfide, tungsten sulfide, zinc sulfide, iron sulfide, either singly or in mixtures; these sulfidic catalysts may also be treated with any one of the known activators such as alkalies, alkali sulfide, etc.

Example 1

A carefully purified water gas is converted at 25 atm. and 250°C. in the presence of a so-called fused iron catalyst. This catalyst is obtained by melting iron (in some cases activating compounds are added) in an oxygen stream and then reducing

the mixed iron oxide which is formed. The compound obtained is almost exclusively composed of saturated and unsaturated hydrocarbons; it is separated, by cooling, from the residual gas: an oily layer separates from the aqueous layer. By further cooling, the oily layer congeals still more, and a dirty brown paste-like mass is obtained which will now be subjected to distillation. The residue boiling above 350° is a deep dark brown, almost black mass, the consistency of which is about equal to that of bee's wax. Twenty liters of this residue are now dissolved in 35 liters triisobutane and the solution is then strongly agitated, at 105°, with 4 kg. of porous "tonsel"\*, for a period of three hours. The gel is then filtered at higher temperature (it is very easily separated from the liquid), and the filtrate is further freed from the last remnants of solvent in vacuo. The residual high boiling mass is found to be extensively cleared when compared to the above mentioned distillation residue; its color is a light white-yellow. The iron content, initially 0.12%, has been decreased to 0.01%.

If various different solvents are used instead of triisobutane, such as triisobutylene, decahydronaphthalene and xylene, the color ranges and degrees of clearing shown in the table below are obtained. The degree of clearing obtained with triisobutane is taken as 10.

Solvent	Color Range	Degree of Clearing
Triisobutylene	Yellow	7
Decahydronaphthalene	Light yellow	8
Xylene	Brown	2 to 3

\*Tonsel = a word probably compounded from "Tonerde" (clay) and "Silica". (Transl.)

The clearing effect, accordingly, is more pronounced, the more the solvent resembles in its characteristics to a saturated aliphatic hydrocarbon.

If one works at the same temperature without solvent and with the same amount of adsorbent clay, the mass is cleared to an extent corresponding, in the scale established above, to about 6. However, in this case the high boiling residue is very difficult to separate from the adsorbent, so that the filtration is extremely slow and the adsorbent, even after the filtration, still contains large amounts of the high boiling residue.

The used adsorbent is extracted successively, for 24 hours each time, with the following solvents: 1) decahydronaphthalene; 2) acetone. With decahydronaphthalene, 1.18 kg. of deep black mass was removed from the gel; with acetone, 0.3 kg. After this treatment, the adsorbent gel can then be re-used for the clearing of synthesis products; it still has about 40% of its original clearing capacity.

If the adsorbent is further boiled with dilute hydrochloric acid, and then washed with water and methanol, it regains 80% of its original activity.

#### Example 2

The conversion of carbon monoxide with hydrogen, described in Example 1 above, is carried out at about 195°; thereby, a product with an average alcohol content of 50% is obtained. Again, this product is distilled and the residue (boiling above 400°) is dissolved in decahydronaphthalene; it is then bleached with silica gel (?) and subjected to hydrogenation at 280° in the



presence of 10% (by wt.) of a copper/barium chromite-containing catalyst for two hours; the hydrogen pressure is kept at 200 atm. Thereby, the color changes to a pure white. The alcohol content (OH No. = 16) is increased, due apparently to ester split (Ester No. = 38). Even after having been used for 5 times in succession, the catalyst showed no appreciable activity decrease.

If, on the other hand, the synthesis product is subjected to hydrogenation without previous adsorptive treatment, the temperature must be maintained at 310°C., all other conditions remaining the same; the hydrogenation product still has a grey green color tone and contains almost no alcohols or other oxygenated compounds. Already after a single conversion, the catalyst has lost so much of its activity that it must be subjected to a regeneration process.

#### Patent Claims

1. Process for the clearing of colored, high boiling component-containing products of the carbon monoxide/hydrogen conversion; the process is characterised by the treatment of the products when diluted with solvents which consist mainly of saturated or not too extensively unsaturated aliphatic or cyclic hydrocarbons.
2. Process for the further clearing of the products after treatment according to Claim 1 above, by treatment with hydrogen in the presence of catalysts.
3. Process for the clearing of synthesis products after Claim 1, characterised by the fact that the used adsorbents may

be regenerated by treatment with organic oxygenated, halogenated or cyclic solvents and, in certain cases, by subsequent treatment with acids; the regenerated adsorbent is then used again for the same purposes.