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ALEXANDER SCHWARCMAN, OF BUFFALO, NEW YORK, ASSIGNOR TO KELLOGG PRODUCTS, INC., OF BUFFALO, NEW YORK, A CORPORATION OF NEW YORK.

CATALYST.

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To all whom it may concern:

Be it known that I, ALEXANDER SCHWARCMAN, a citizen of the United States, residing at Buffalo, in the county of Erie and State of New York, have invented certain new and useful Improvements in Catalysts, of which the following is a specification.

This invention relates to catalysts and methods of making the same; and it comprises a method of making a catalyst suitable for simultaneous purification, decolorizing, filtering and hardening of oils, either animal or vegetable, wherein good white quartz is ground to a fine mesh, say a fineness of 120 mesh, boiled for a time, say two hours, with a solution of caustic soda, washed, mingled with a certain amount of fullers' earth of good decolorizing power, advantageously in a somewhat smaller amount, and the mixture impregnated with a solution of a nickel salt, such as nickel nitrate, made alkaline with caustic soda, washed and reduced at a low temperature, say 200°–300° C., the caustic soda used for the second treatment advantageously containing a small amount of a nitrogenous colloid body, such as wool; and it also comprises as a new composition of matter a non-sliming, decolorizing hydrogen-adding catalyst of readily permeable texture composed of a mixture of very fine sharp quartz fragments and fullers' earth, holding finely divided nickel firmly and fixedly; all as more fully hereinafter set forth and as claimed.

In the hardening of oils, it is a common practice to treat the oil with hydrogen in the presence of freshly reduced nickel; this nickel being used in different physical forms, as powder, as colloidal solution, as thin leaves, etc. Very frequently, the nickel is used with a carrier or diluent, such as kieselguhr, charcoal, etc. The hardening is conducted at a rather high temperature and is apt to result in some darkening of the oil—it has no beneficial action on the color. After the hardening is complete, or has been carried to the extent desired, the nickel must of course be removed; and in practice this removal is somewhat hard to effect. This is due partly to the existence of some or all of the nickel in a colloidal form, rendering filtration with removal of nickel difficult. To some extent, it is due to the presence of nickel soaps in solution or quasi-solution and these are also difficult of removal. For the purpose of lessening these difficulties, and also to secure an extensive surface of nickel, etc., it is desirable to use a carrier, some other material by which the finely divided nickel is held.

In decolorizing oil it is common to use fullers' earth. Fullers' earth is a type of clay which has strong adsorptive powers for coloring matter. It is used as a decolorizing agent with all kinds of oils; not only vegetable oils and animal oils but also mineral oils. It is a material of very fine texture; it being indeed to its fineness and the extensive surface thereby offered that it owes much of its decolorizing power. But because of this fineness in texture it is somewhat difficult to cause fluid, like oil to pass rapidly through it; it is, so to speak, a slow filtering and draining material. In practice it is often used for decolorizing oils before or after the hardening operation. It has been proposed as a carrier for nickel in the hardening operation itself; but since fullers' earth is rather fine in its texture the nickel used with the earth as a carrier is apt to slime off unless special precautions are adopted. In another application Serial No. 185,917 I have described and claimed a method of making a compound catalyst with the use of fullers' earth in which these difficulties are obviated; the nickel being deposited in the fullers' earth in a particular way in which it is fixedly held even though it be in the state of fine subdivision which is necessary for the greatest efficiency in hydrogenation. In so doing a material is produced which has the power of hardening oil and also of decolorizing it. With such a material because of the way it is made hydrogenation may be performed at relatively low temperatures at which not much darkening takes place, and the decolorizing power of the fullers' earth is sufficient to take care not only of the slight darkening which may occur in the hydrogenation but also of the natural coloring matter of the oil itself. In producing such an article I first treat the fullers' earth with a soluble nickel salt. The nickel salt is more or less taken up or adsorbed by the fullers' earth. The material is next treated with a caustic soda solution containing a small amount of dissolved nitrogenous colloid matter, such as wool, glue, casein, etc. Under the influence of the colloid, the oxid of nickel is deposited in the

fullers' earth in a particular relation; in a colloid form. This particular relation subsists after heating and reduction although the nitrogenous colloid disappears as such during the incident heating. The final product retains its nickel against sliming off, hydrogenates at a low temperature and decolorizes very effectively.

Another very useful carrier for nickel, as I have found, can be made from rock quartz; the quartz being ground to a fine powder of, say, between 20 mesh and 120 mesh. Quartz breaks with an irregular, more or less conchoidal fracture; and however far the reduction in size be carried the ultimate particles are still of this character. Reduced nickel clings to these surfaces very well. It is better that the quartz be first heated to a high temperature, say 1000° F., or thereabout and then comminuted. In so doing comminution is rendered easier and the character of the final material is much improved; possibly by a partial conversion of the quartz into tridymite and possibly by the production of other physical changes. Quartz so treated yields a material which, as compared with ordinary quartz powder, may be described as in a measure fluffy. Because of the irregular jagged shape of the ultimate fragments a compound catalyst made by treating the quartz powder with a nickel salt and then with caustic soda to precipitate nickel oxid on the surfaces with final reduction gives a material particularly adapted for treating oil. It remains suspended very well during the agitation and settles cleanly on quiescence, but does not pack down to a hard impervious dense cake. From the settled material the oil is readily removed by suction, draining, etc., because of the open texture given by the shape of the fragments. The quartz is best thoroughly extracted with caustic alkali, such as caustic soda solution, prior to its use in order to remove alkali-soluble bodies.

I have found that a very useful catalyst for treating oils may be made by combining the invention of the said acknowledged case with that just described. By using as the carrier for the nickel a composition which is partly fullers' earth and partly fine quartz powder, a composition is obtained which when dried preliminarily to reduction does not cake or harden but remains loose in texture. After impregnation with nickel, precipitation of the nickel and reduction, a compound catalyst is obtained which has similar advantageous properties in the treatment of oil. It settles better than the catalyst made with the fullers' earth alone, and residual oil is more readily withdrawn from the presscake. The proportion of fullers' earth and quartz may be as desired for the particular operation in which it is to be used. As a rule, I find that a ratio of 80 parts of fullers' earth and 20 parts of fine ground quartz works well. For a more pervious product the proportion of fullers' earth may be reduced to, say, 60 parts and that of quartz raised to, say, 40 parts.

In using as the carrier a mixture of fullers' earth and fine quartz, the use of wool or the like nitrogenous colloid in the caustic soda employed as a precipitant is advantageous. The presence of the organic nitrogenous colloid in the caustic soda much improves the product. I therefore customarily employ it.

In a practical embodiment of the present process I take a good white quartz and crush and grind it to a fine texture. I find it advantageous to have it all pass through a screen at least as fine as 80 to 120 mesh. In order to have it absolutely clean I may heat this fine powder with various chemicals, acids and the like, but ordinarily it is sufficient to treat it with caustic soda. I find it desirable, ordinarily, to boil the fine powder with a caustic soda solution of about 20° B. for two or three hours. After heating with the soda solution, the quartz is next washed clean and dried. With this dried material I incorporate fullers' earth in the desired proportion. The mixture of crushed quartz and fullers' earth is next treated to impregnate it with nickel. For this purpose I can use various soluble nickel salts but I prefer the nitrate. However nickel sulfate and other nickel salts may be used.

Impregnation with nickel may be in any of a number of ways. The carrier may be impregnated with a concentrated solution of nickel salt; this solution being in the amount that the mineral matters will take up readily. But I may use weaker solutions and evaporate the mixture somewhat to secure a concentrated solution in the pores. The use of a concentrated solution in this manner however is not necessary. If the mixture of fullers' earth and quartz be stirred up with the solution of nickel nitrate, adsorption may be relied upon to transfer sufficient of the dissolved salt of nickel to the pores and surfaces of the carrier. The impregnated carrier, however made, is next treated with a solution of caustic soda which forms nitrate of soda which remains in solution and a precipitated hydrate of nickel in the pores. Or impregnation with nickel and precipitation may be in the same solution; the compound carrier being stirred up with a suitable solution of a nickel salt and caustic soda added directly to the mixture. After precipitation, the compound catalyst is washed to remove the soda salts, is dried and is then reduced at a low temperature. It is best, as stated, to use a small amount of some organic nitrogenous colloid such as wool dissolved in the caustic soda solution. Instead of wool, leather, glue, hair, gelatin, casein

and egg albumen may be employed in about the same quantity. By so doing the physical character of the precipitate in the pores and its relation to the surfaces of the carrier are so changed that the nickel is fixedly held. This effect persists after drying and reducing the catalyst. A solution of 2 parts of ordinary wool in a caustic soda solution containing 25 to 30 parts of soda in 200 parts of water, makes a good precipitant. I find that the decolorizing effect of fullers' earth so treated, that is, the power of removing the color giving constituents of oil, is not forfeited; indeed it is somewhat enhanced by the treatment.

In a specific embodiment of the present invention, I may suspend 100 parts of the mixture of fullers' earth and quartz in 1,000 parts of water by agitation and add 100 parts of commercial nickel nitrate dissolved in 300 parts of water. The temperature of the mixture is brought to about 180° F. and to it is added a precipitant made by dissolving 27.5 parts of caustic soda in 200 parts of water and adding 2 parts of wool. The reaction forms colloidal nickel hydrate which is taken up and firmly held by the mineral matter. The mineral matter may now be washed by decantation or filtered off, pressed and dried. It is next reduced. This reduction need not be at a particularly low temperature; temperatures of 500° to 600° C. giving good results. Lower temperatures may be used.

In an alternative method, the mineral matters are impregnated with about the amount of nickel nitrate solution which will be taken up, treated with a caustic soda solution which may contain wool, washed and dried. Washing should be continued until the alkaline reaction disappears. Drying may be in any usual manner as may reduction by hydrogen. During the heating and reduction the organic colloid disappears but the nickel and mineral matters remain in their advantageous relation.

Instead of fullers' earth, I may use other decolorizing agents; but I find that ordinary fullers' earth is the best for the present purposes. Other decolorizing powders, such as some of the vegetable carbons, may be used, but they have no advantage over fullers' earth. Kieselguhr and other porous mineral powders may be used but they do not have the decolorizing action here described.

The catalyst of the present invention may be used in connection with oil to be hardened in any of the usual apparatus and by any of the usual processes. The activity of the nickel however is so great in this preparation that lower temperatures than usual may be used in hardening. Even as low as 300° F., may be employed, especially if the hydrogen be used in such a way as to produce a relatively fine emulsion. With the very fine hydrogen emulsion, the minute bubbles tend to be taken up or adsorbed by the pores of the carrier and are in position to exercise a maximum activity upon the oil and the nickel. By this operation at low temperature is gained the advantage of not darkening the material as much as is incident to the operation at the usual higher temperatures.

Whether the temperature be low or high, the fullers' earth exercises its decolorizing action concomitantly with the hardening action of the nickel; and the darkening, in the case of high heat, is counteracted by the action of the fullers' earth. After a charge of oil has been hardened and decolorized by the present catalyst, the catalyst may be used with a fresh charge of oil. This reuse may be in methodical way, partially used catalyst being used with fresh oil and once treated oil exposed to the action of fresh catalyst.

I find that as a matter of practice the activity of the nickel and the decolorizing power of the fullers' earth last for about the same length of time; that is, at a time when the high activity of the nickel begins to lessen, the decolorizing power of the fullers' earth also tends to become exhausted. At this time, the catalyst may be removed and extracted to regain adhering oil. It may be then extracted with nitric acid to regain the nickel and the fullers' earth discarded.

Instead of nickel I may use palladium, cobalt, etc., as catalyst, but I regard nickel as particularly well adapted for the present purposes. Instead of using caustic soda I may of course use caustic potash. Carbonate of soda (sodium carbonate) and carbonate of potash (potassium carbonate) are good precipitants but do not dissolve wool, hide, leather, etc., with as much facility as the caustic alkali. They do however dissolve casein and glue quite as well.

As to the exact action of the wool or other organic colloid in the precipitating solution, I am not aware, but the result is probably the precipitation of nickel oxid in a highly colloid form; a form in which it is taken up and held tenaciously in and on the pores and surfaces of the catalyst which tend to adsorb vigorously colloid matters; particularly those of the fullers' earth. This colloid condition of the nickel oxid may or may not resist after the heating incident to reduction; but it is probable that the mutual relation of the metallic nickel and surfaces of the grains of catalyst is the same after the heating as that of the nickel oxid and the surfaces before the heating. The nickel oxid being taken up by the fullers' earth in a colloid form is probably very uniformly distributed over the surfaces of the carrier; a fact to which the unusual activity of the preparation is probably due. Other things

being equal, the activity of any nickel preparation is usually proportionate to its state of subdivision.

In this process I find that the treatment improves the quality of the fullers' earth as a decolorizing agent; this being due to the caustic soda employed in precipitation. After the treatment with caustic soda the fullers' earth is changed somewhat in its physical consistency, becoming so to speak, fluffier or lighter. In the presence of the finely divided quartz the advantage of this fluffiness or lightness of texture is retained while at the same time the catalyst as a whole presents the advantages given it by the quartz of easy disintegration of the presscake and ready removal of the oil after the operation is complete. A caustic soda treatment of both the quartz and the fullers' earth is advantageous as freeing both to a large extent of the constituents which, and especially in the case of fullers' earth, tend to give the oil an earthy taste on treatment. The caustic soda used in precipitation of the nickel tends to extract some alkali-soluble matters but it is better to use the preliminary extraction with caustic soda solution as well. The mixture of quartz and fullers' earth may be so extracted with soda after it is made; or either component may be separately extracted. In the extraction the mineral matter is boiled with a strong solution of caustic soda and then washed thoroughly; thoroughly enough to remove the taste of the caustic soda. It is convenient to wash until the effluent wash water does not blue litmus. Washing may be in a filter press or any other usual way. The so treated material may then be used to produce a catalyst in any of the ways hereinbefore described. In so doing, the material is subjected to two treatments with caustic soda; although as a matter of fact the first treatment removes all the objectionable constituents.

In a practical embodiment of my method using a preliminary extraction 100 parts of quartz or of fullers' earth or of a mixture of the two may be suspended in 500 parts of a solution of caustic soda of 20° Bé. which contains between 14 and 15 per cent. NaOH. The mixture is brought to a boiling temperature and kept boiling for about an hour. The mineral matter may then be washed by decantation or in a filter press until all the soluble caustic alkali is removed. The mineral matter so prepared is then suspended in 1000 parts of water and 100 parts of nickel nitrate added in solution in 300 parts of water. The mixture having been brought to a boil to permit the mineral matter to take up the nickel salt, a solution of 27.5 parts of NaOH dissolved in 250 parts of water is added. This precipitating solution, like the precipitating solutions previously described, is best first treated by dissolving two parts of wool or other colloid nitrogenous matter therein. After adding the soda, the mineral matter is again washed by decantation or in a filter press until no soluble salts remain. The precipitate is then pressed, dried and reduced with hydrogen.

This preliminary treatment with caustic soda to free it of all bodies soluble in caustic soda gives a compound catalyst which is much more sensitive than that obtained with carriers not so treated. It is so sensitive that hydrogenation may be performed at much lower temperatures than those usually employed and in less time. In some cases the reduction in time required for hardening to the same degree is 50 per cent. The usual nickel catalyzers require temperatures between 320 and 400° F. but with a carrier which has been previously treated in the manner described not only are the other advantages of my invention obtained but hydrogenation can be performed at 260° F.; which is a very convenient temperature and a temperature at which the development of color to be removed by the fullers' earth is much lessened. Because of this little development of color at the low temperature used, the decolorizing activity of the fullers' earth component is not quickly exhausted; the present compound catalyst if used at these low temperatures may be employed for a considerably longer time.

What I claim is:—

1. As a catalyst, a mixture of fine ground quartz and fullers' earth carrying finely divided nickel.

2. As a catalyst, a mixture of fine ground roasted quartz and fullers' earth carrying finely divided nickel.

3. As a catalyst, a mixture of fine ground quartz and fullers' earth carrying finely divided nickel, said mixture being free of alkali-soluble matters.

4. As a catalyst, a mixture of fine ground roasted quartz and fullers' earth carrying finely divided nickel, said mixture being free of alkali-soluble matters.

5. As a catalyst, a mixture of fine ground quartz and fullers' earth carrying finely divided colloidal nickel.

6. As a catalyst, a mixture of fine ground roasted quartz and fullers' earth carrying finely divided colloidal nickel.

In testimony whereof, I affix my signature hereto.

ALEXANDER SCHWARCMAN.