UNITED STATES PATENT OFFICE.

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CATALYST AND METHOD OF MAKING THE SAME.

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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 and Methods of Making the Same, 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 and hardening of oils, either animal or vegetable, wherein fullers' earth or other decolorizing powder is impregnated with a solution of a nickel salt, is treated with an alkaline precipitant containing a nitrogenous colloid such as wool, and is then reduced to give active nickel; and it also comprises as a new composition of matter a non-sliming decolorizing hydrogen-adding catalyst composed of fullers' earth and finely divided nickel firmly and fixedly held therein; 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.

Fullers' earth is of course a good decolorizing agent for oils of all kinds, both mineral oils and animal and vegetable oils. In practice, it is often used before or after the hardening for the purpose of decolorizing the oil. It has been proposed as a carrier for the nickel in the hardening itself but fullers' earth is rather fine in its texture and the nickel is apt to slime off. For this reason other carriers, such as kieselguhr and charcoal, have been employed. With these carriers also the difficulty, noted ante, of sliming off also occurs; being responsible, in part, for the difficulty in freeing the oil of nickel after the operation.

I have found that I can deposit the nickel in fullers' earth in a particular way and obtain a carrier-held catalyst in which the nickel 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, I produce a compound catalyst which has not only the hardening property but also the decolorizing property of fullers' earth; and I am enabled to decolorize and harden in one operation instead of doing it, as is usual, in two. For this purpose, I first impregnate the fullers' earth with a soluble nickel salt, which is, advantageously, the nitrate. Other salts may be used but the nitrate I regard as the best. I may use it in the form of a concentrated solution of the amount of nickel required; the solution being in the amount that fullers' earth will take up readily. Weaker solutions in greater volumes may be employed and in such event the mixture may be dried after the impregnation to secure the presence of a concentrated solution in the pores. Or the fullers' earth may be simply suspended in a solution of nickel nitrate, absorption being relied on to transfer the dissolved salt of nickel to the pores and surfaces of the earth. The impregnated fullers' earth 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. If the caustic soda is used alone, however, I find that the product does not have the described properties. On drying and reduction a catalyst is obtained having the nickel not permanently retained. But by dissolving in the caustic soda solution a small amount of almost any organic nitrogenous colloid, the physical character of the precipitate in the pores and its relation to the fullers' earth 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. After precipitation, the compound catalyst is washed to remove the soda, dried and is then reduced at a low temperature. 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 commercial fullers' earth 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 fullers' earth. The fullers' earth may now be washed by decantation, 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. Instead of wool, leather, glue, hair, gelatin, casein and egg albumen may be employed in about the same quantity.

In an alternative method, the fullers' earth is impregnated with about the amount of nickel nitrate solution which it will take up, treated with a caustic soda solution containing a dissolved organic nitrogenous colloid body, washed and dried. Washing should be 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 fullers' earth remain in their advantageous relation.

Instead of fullers' earth, I may use other decolorizing agents; but I find that ordinarly 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 fullers' earth and colloidal nickel 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 a very fine hydrogen emulsion, the minute bubbles tend to be taken up or adsorbed by the pores of the fullers' earth 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 use may be in methodical way, partially used catalyst being used with fresh oil.

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 catalysts 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 the pores of the fullers' earth which tend to adsorb vigorously colloid matters—a fact to which a large part of the utility of fullers' earth is due. This colloid condition of the nickel oxid may or may not persist after the heating incident to reduction; but it is probable that the mutual relation of the metallic nickel and surfaces of the fullers' earth grains 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 fullers' earth; 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. It flows and distributes through the oil much better than untreated fullers' earth; and it is free to a large extent of the constituents which tend to give oil an earthy taste on treating it with fullers' earth. These advantages are particularly marked in the embodiment of my invention where the fullers' earth is treated with the nickel salt and subsequently with caustic soda in the presence of a large amount of water which is separated prior to drying and reducing.

These advantages are so marked that I find in practice it is desirable to give the fullers' earth, prior to any other operation, a washing with caustic soda. In so doing I take the fullers' earth and boil it with a strong solution of caustic soda and then wash it 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 fullers' earth may then be used to produce a catalyst in any of the ways hereinbefore described. In so doing, the fullers' earth 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 fullers' earth may be suspended in 500 parts of a solution of caustic soda of 20° Bé. or between 14 and 15 per cent. NaOH. The mixture is brought to a boiling temperature and kept boiling for about an hour. The fullers' earth may then be washed by decantation or in a filter press until all the soluble caustic alkali is removed. The fullers' earth 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 fullers' earth to take up the nickel salt, a solution of 27.5 parts of NaOH dissolved in 250 parts of water is added. This solution, like that previously described, is best first treated by dissolving two parts of wool or other colloid nitrogenous matter therein. The fullers' earth 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.

Fullers' earth which has been first treated with caustic soda in the manner described to free it of all ingredients soluble in alkalis, yields a catalyzer which is more sensitive than that obtained with fullers' earth 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 fullers' earth 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. The nickel catalyzer so obtained is unusually long lived and since the amount of color to be removed by the fullers' earth is lessened by the low temperature the compound catalyst may be employed for a longer time.

I find that the described preliminary treatment of a carrier with a strong caustic soda solution is useful in producing compound materials useful in both decolorizing and hydrogenating and containing nickel in a very sensitive form. As the base of these compound catalyzers I may use in lieu of fullers' earth other porous materials having a strong adsorptive power for coloring matter, such as the vegetable carbon preparations now known on the market as "decolorizing carbons."

What I claim is:—

1. The process of making a non-sliming decolorizing catalyst which comprises impregnating a decolorizing powder with a nickel salt, precipitating the nickel in the pores of the material with a solution carrying a dissolved nitrogenous organic colloid, drying and reducing.

2. The process of making a non-sliming decolorizing catalyst which comprises impregnating a decolorizing powder with a nickel salt, precipitating the nickel in the pores of the material with a solution carrying dissolved wool, drying and reducing.

3. The process of making a non-sliming decolorizating catalyst which comprises impregnating fullers' earth with a nickel salt, precipitating the nickel in the pores of the material with a solution carrying a dissolved nitrogeneous organic colloid, drying and reducing.

4. The process of making a non-sliming decolorizating catalyst which comprises impregnating fullers' earth with a nickel salt, precipitating the nickel in the pores of the material with a solution carrying dissolved wool, drying and reducing.

5. The process of making a non-sliming decolorizing sensitive catalyst which comprises treating a decolorizing powder with a boiling solution of caustic soda, freeing from alkali, impregnating with a nickel salt, precipitating the nickel in the pores of the

material with a solution carrying a dissolved nitrogenous organic colloid, drying and reducing.

6. The process of making a non-sliming decolorizing sensitive catalyst which comprises treating a decolorizing powder with a boiling solution of caustic soda, freeing from alkali, impregnating with a nickel salt, precipitating the nickel in the pores of the material with a solution carrying dissolved wool, drying and reducing.

7. The process of making a non-sliming decolorizing catalyst which comprises washing fullers' earth with a boiling solution of caustic soda, freeing from alkali, impregnating with a nickel salt, precipitating the nickel in the pores of the material with a solution carrying a dissolved nitrogenous organic colloid, drying and reducing.

8. The process of producing highly sensitive nickel catalysts which comprises boiling a suitable porous carrier material in a strong solution of caustic soda until all alkali-soluble matters are removed, removing the alkali by washing, impregnating with a nickel compound and reducing.

9. The process of producing highly sensitive nickel catalysts which comprises boiling fullers' earth in a strong solution of caustic soda until all alkali-soluble matters are removed, removing the alkali by washing, impregnating with a nickel compound and reducing.

10. As a new catalyst, a porous pulverulent material having high adsorbing power for coloring matters and carrying colloidal nickel in its pores, said material being free of alkali soluble substances.

11. As a new catalyst, fullers' earth carrying colloidal nickel in its pores.

12. As a new catalyst, fullers' earth freed of alkali-soluble matters and carrying colloidal nickel in its pores.

In testimony whereof, I affix my signature.

ALEXANDER SCHWARCMAN.