

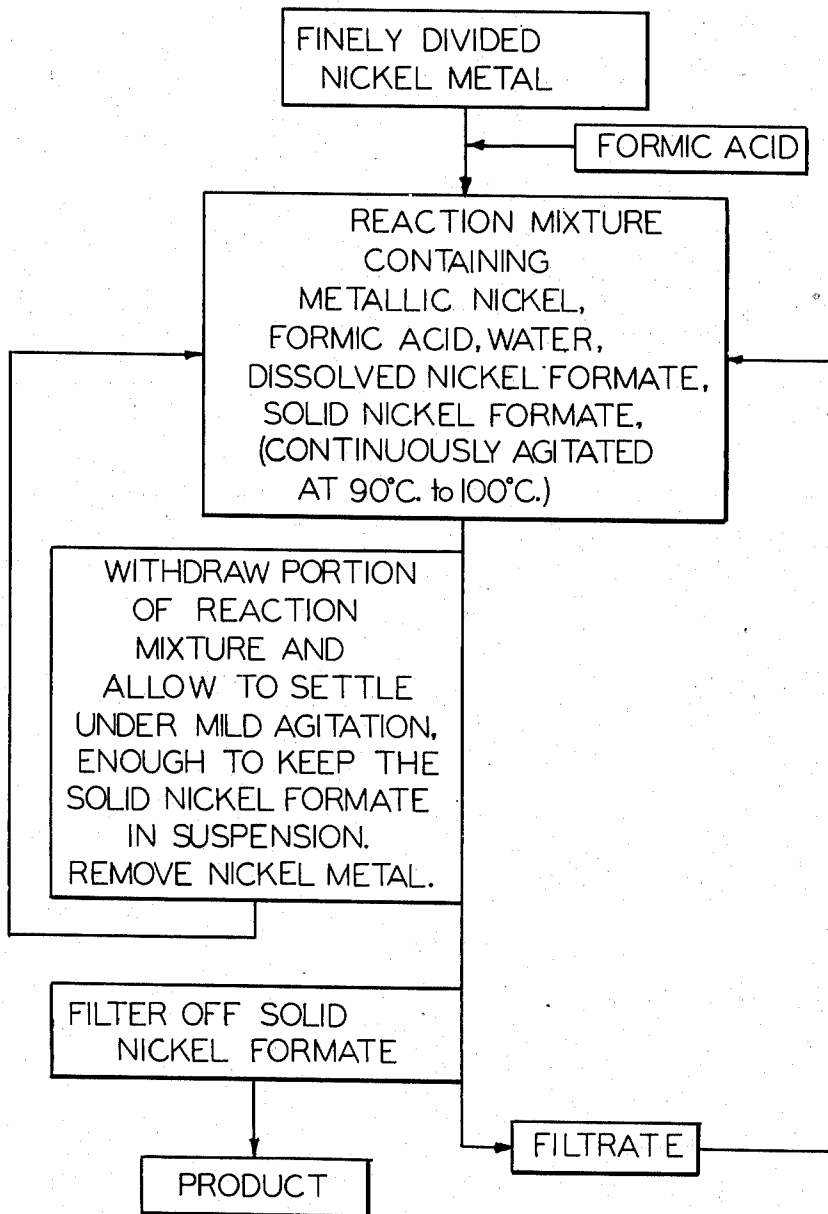
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MANUFACTURE OF NICKEL FORMATE

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MANUFACTURE OF NICKEL FORMATE

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This invention relates to a method of producing nickel formate by dissolving nickel metal in formic acid.

Nickel formate is used in large quantities in the catalytic hydrogenation of oils, especially vegetable oils in the manufacture of margarine and vegetable shortenings. Nickel metal is the ultimate catalyst, but the formate is reduced to metallic state in the hydrogenation reaction and may therefore be added, instead of reduced nickel, to the charge of oil to be hydrogenated. Notwithstanding the large use of nickel formate for hydrogenation, the prevailing method of preparation has continued for perhaps thirty years to involve precipitation of nickel carbonate from nickel sulfate solution by the use of soda ash and reaction of the carbonate with formic acid. Nickel formate thus commercially prepared is contaminated with by-product salts to an extent that it is seldom much, if any, above 99% purity.

While it is common practice to produce metal salts of strong acids by direct attack of the acid on the metal in aqueous solution, it has not been supposed that such a corrosion-resistant metal as nickel could be dissolved in such a weak acid as formic acid at a rate such as would be adequate for production of the salt on a commercial basis. Mellor (vol. 15, page 147) reproduces a diagram from *Chemiker-Zeitung* (Krulla, vol. 54, pages 429-431, 1930) which indicates an exceedingly slow rate of corrosion of nickel by formic acid. Indeed Krulla indicates that acetic acid is several times more corrosive to nickel than formic acid. The International Nickel Company, in a publication entitled "Corrosion," published in 1944 gives the rate of corrosion of nickel by formic acid as four-thousandths of an inch per year. The same publication indicates corrosion of metallic nickel by 90% formic acid to be eighteen-thousandths of an inch per year at the temperature of boiling water. "Uhlig's Corrosion Handbook" (1948), page 260, indicates that acetic and formic acids are moderately corrosive to nickel as compared with other organic acids. Considerable quantitative information is given in regard to acetic acid indicating corrosion rates under varying conditions varying from a few thousandths of an inch per year to thirty-four hundredths of an inch per year for 75% acid under the combined effect of aeration and agitation. Formic acid should, according to the literature referred to, be less corrosive than acetic acid. The above literature references are concerned with corrosion and evidently were based upon studies wherein the investigator was chiefly in-

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terested in avoiding the harmful effects of corrosion rather than any possibility of manufacture of metal salts.

I have now discovered that it is feasible to produce nickel formate by the action of formic acid on nickel metal under suitable conditions.

Attempts to produce nickel formate by adding powdered nickel metal to aqueous formic acid solutions at various temperatures on a beaker scale indicated that a coating would be formed which would soon stop the reaction or slow it down to an unsatisfactory rate. At an elevated temperature, the reaction proceeded at a higher rate, but a hard cake was soon formed in the bottom of the beaker. An attempt was made to overcome this situation by passing aqueous formic acid solution through a reaction tube containing the nickel metal at such a rate that the solution would not become saturated with respect to nickel formate, and then separating the nickel formate from the resulting solution, returning the liquor with some addition of formic acid for further contact with the nickel metal. The amount of distillation necessary to carry out this procedure proved excessive, the weight of nickel formate recovered being only about 3% of the weight of liquor which had to be evaporated.

Inasmuch as the problem of the solid nickel formate coating on nickel metal could not be avoided by keeping the formate in solution, at least not without excessive distillation cost, further investigation was undertaken which led to the discovery that if the reaction temperature is maintained in the region from 90° C. to 110° C., and agitation is continuous, the particles of nickel formate do not adhere to the particles of nickel metal, and, because of the much higher specific gravity of the nickel metal it is possible to separate it from the nickel formate.

Accordingly, I am able to produce nickel formate from nickel metal by establishing a reaction mixture wherein formic acid in aqueous solution is brought into contact with nickel metal at a temperature in the range from 90° C. to 110° C. with continuous agitation, withdrawing a portion of the reaction mixture which, on account of the agitation, contains all the components thereof, separating from such withdrawn portion, by physical means, the nickel metal, normally contaminated with nickel formate, and the nickel formate in condition substantially completely free of nickel metal, returning the resulting parts of such withdrawn portion to the reaction mixture with the exception of the nickel formate, and adding to the reaction mixture

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formic acid, nickel metal, and water, sufficient to compensate for such amounts of these materials as are removed as product or otherwise and not returned as above indicated. The physical means of separation referred to may be a settling procedure wherein the liquor is agitated sufficiently to suspend the nickel formate, but not sufficiently to suspend the particles of nickel metal. Under such conditions the nickel metal will concentrate at the bottom together with some adherent nickel formate while the nickel formate will be distributed through the liquid, permitting the latter to be drawn off and filtered for the recovery of nickel formate. After the nickel formate slurry has been drawn off, it may be allowed to settle and the liquor decanted off instead of filtering. Again, the separation of the components of the withdrawn portion of the reaction mixture may be accomplished by the use of a centrifuge of continuous or other type whereby greater speed can be achieved than with the simpler sedimentation method. It is of greatest importance that there be no long-continued interruptions in the agitation of the reaction mixture. Some interruption can be tolerated and, with short intervals, intermittent agitation can be employed. Agitation which is characterized by interruptions of only such short duration that no substantial agglomeration takes place is to be considered as comprehended within the term "continuous."

The accompanying drawing is a flow-sheet diagram illustrating the present preferred embodiment of the invention.

The nickel metal employed should be finely-divided, but it is not essential that all the particles be in the same state of subdivision. A commercial product known as "steam shattered shot" can be very successfully used. This material is a mixture of particle sizes varying from perhaps $\frac{1}{8}$ of an inch in diameter to powder or dust. The major portion would pass through a 30 mesh screen, and a substantial portion through a 100 mesh screen. Very little, perhaps less than 10%, would remain on a 4 mesh screen. It is not essential that a material of such fine state of subdivision as steam shattered shot should be used; however, in order to secure a satisfactory rate of nickel formate production, the major portion of the particles of metal should pass a 30 mesh screen, and at least 90% should pass a 4 mesh screen.

The effect of agitation is related not only to prevention of cementation of the particles of nickel formate on the particles of nickel metal and the consequent formation of agglomerates, but also to the rate of reaction, the relative movement between the solution and the metallic surface being essential to keep the metal particles clean of reaction product which would slow down the reaction as well as causing cementation of the particles into agglomerates. It is not essential that the agitation be extremely vigorous, so long as it is continuous, and such agitation as is produced by boiling the reaction mixture may be satisfactory. Even a lesser degree of agitation may be adequate but a gentle boiling of the reaction mixture accompanied by mechanical stirring is preferable.

The range of concentration of formic acid which can be employed is rather wide. A reasonable rate of reaction can be had with solutions as dilute as 30% by weight and up to 100%, but the preferred concentration range is from 60% to 85%, based on the combined weight of formic acid and water present in the reaction mixture.

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By establishing a reaction mixture from which material is continuously removed, or is removed in successive portions, and returning to such reaction mixture all the content of the removed material except the nickel formate, there results the possibility of merely adding from time to time, or continuously, a replenishing amount of nickel metal and of formic acid, so that any relatively large particles of nickel will simply, in effect, remain in the reaction mixture until consumed. Such large particles will naturally require a longer time for complete consumption, but if the proportion is not too large, the process may be operated at a satisfactory rate without undue build-up of relatively large particles of metal. As above indicated, the particle size of the metal is not sharply critical and, with large enough equipment and adequate agitation, any size pieces of nickel can be used, but particle size is related to the rate of reaction, so that, for practical purposes, the nickel should be finely divided.

By reference to the drawing, it will be seen that formic acid solution is caused to react with metallic nickel to an extent that the liquid portion of the reaction mixture will not dissolve all of the nickel formate, and solid nickel formate precipitates in the reaction mixture. Under the essential conditions as above indicated, the reaction will go beyond saturation of the solution with nickel formate, nickel formate being formed at the surface of the metal, taken into solution, and precipitated out again from solution whereby the solid portion of the reaction mixture becomes a mixture of solid nickel formate and solid nickel metal. Continuous agitation prevents the solution and precipitation from taking place at one and the same point as would happen under conditions of no agitation. When the proportion of solid nickel formate has built up in the reaction mixture to a practical extent, I then remove a portion of the reaction mixture either continuously or in successive removals, and separate the nickel formate therefrom in the manner above indicated. The portion of the reaction mixture subjected to separation can be the entire amount, but I consider it more practical to remove it continuously, and continuously subject the removed portion to separation as indicated. I find it better to conduct the separation outside the reaction mixture (except for possible rough screening of the withdrawn portion) since the conditions of the reaction should result in approximately homogeneous conditions throughout the reaction mixture. The nickel metal in the reaction mixture should be kept thoroughly admixed with the liquid and the solid nickel formate whereas, during the separation procedure, the conditions must favor concentration of the nickel metal particles to a degree to permit separation. Accordingly, I prefer to withdraw slurry continuously from a homogeneous reaction mixture and separate the nickel metal from the slurry so withdrawn by physical means based upon its higher specific gravity (or possibly upon its magnetic properties) and return it to the reaction mixture. I then separate the solid nickel formate from the liquid by filtration, sedimentation, or the like, and return the liquid to the reaction mixture, all as indicated in the drawing. Continuous operation of the various steps in the process is desirable, however intermittent operation of some or all is possible and is to be considered the equivalent of strictly continuous operation and comprehended in the word "continuous."

The following specific example will serve to illustrate the invention:

Example I

Into a suitable reaction vessel were introduced 120 parts by weight of nickel in the form of steam shattered shot, and 200 parts by weight of 85% formic acid. The temperature was brought up to the boiling point of the mixture, and boiling was continued for a period of four hours, the mixture being vigorously agitated by a propeller-type stirring device. At the end of four hours the agitator was stopped. The nickel was allowed to settle under slight agitation, and the suspension of nickel formate was decanted off and filtered.

It will be seen that by returning the filtrate to the reaction vessel together with additional portions of nickel metal and formic acid, the conditions are suitable for the succeeding batch. The amount of nickel metal dissolved was 10.5 parts by weight, amounting to 8.75% of the batch. The product showed on analysis 99.9 per cent of nickel formate dihydrate.

Having thus described my invention, what I claim is:

1. A process for producing nickel formate comprising establishing a reaction mixture wherein finely-divided nickel metal is brought into contact with formic acid at a temperature within a range from 90° C. to 110° C., continuing the reaction, with continuous agitation, until a substantial proportion of the nickel has reacted with the formic acid to produce a substantial quantity of nickel formate over and above the amount required to saturate the reaction mixture, whereby the reaction mixture contains a substantial proportion of solid nickel formate, subjecting at least a portion of the resulting reaction mixture to mechanical separation for removal therefrom of the unreacted nickel metal and separating solid nickel formate from the resulting slurry.

2. A process for producing nickel formate comprising establishing a reaction mixture wherein finely-divided nickel metal is brought into contact with formic acid in aqueous solution at a temperature within a range from 90° C. to 110° C., continuing the reaction with continuous agitation until a substantial proportion of the nickel has reacted with the formic acid to produce a substantial quantity of nickel formate over and above the amount required to saturate the reaction mixture, whereby the reaction mixture contains a substantial proportion of solid nickel formate, subjecting at least a portion of the resulting reaction mixture to mechanical separation for removal therefrom of the unreacted

nickel metal, separating the solid nickel formate from the resulting slurry and returning to the reaction mixture the liquid and metallic nickel content of said separated portion.

3. In a continuous process for producing nickel formate, establishing a reaction mixture in a reaction vessel, said reaction mixture being composed of water, formic acid, nickel metal, and nickel formate, the liquid portion of said mixture being saturated with respect to nickel formate, continuously agitating said mixture, continuously withdrawing from said reaction vessel a slurry containing each of said components of the reaction mixture, separating from said slurry a fraction principally composed of metallic nickel and returning it to the reaction vessel, and then separating from the remainder of said slurry a fraction principally composed of solid nickel formate substantially free of metallic nickel, and returning the liquid portion of said slurry and replenishing amounts of nickel metal and formic acid to said reaction vessel.

4. In a continuous process for producing nickel formate, establishing a reaction mixture in a reaction vessel, said reaction mixture being composed of water, formic acid, nickel metal in a state of subdivision to pass 90% through a 4-mesh screen and more than 50% through a 30-mesh screen, and nickel formate, the liquid portion of said mixture being saturated with respect to nickel formate, continuously agitating said mixture, maintaining the temperature of the reaction mixture at from 90° C. to 110° C., the concentration of formic acid being from 60% to 85% of the combined weight of water and formic acid, continuously withdrawing from said reaction vessel a slurry containing each of said components of the reaction mixture, continuously separating from said slurry a fraction principally composed of metallic nickel and returning it to the reaction vessel, and continuously separating from the remainder of said slurry a fraction principally composed of solid nickel formate substantially free of metallic nickel, and continuously returning the liquid portion of said slurry and replenishing amounts of nickel metal and formic acid to said reaction vessel.

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