Dec. 18, 1945. L. V. HORN 2,391,050

PROCESS FOR EXTRUDING ACID-ACTIVATED MONTMORILLONITE CLAY

Filed Jan. 25, 1944 2 Sheets-Sheet 1

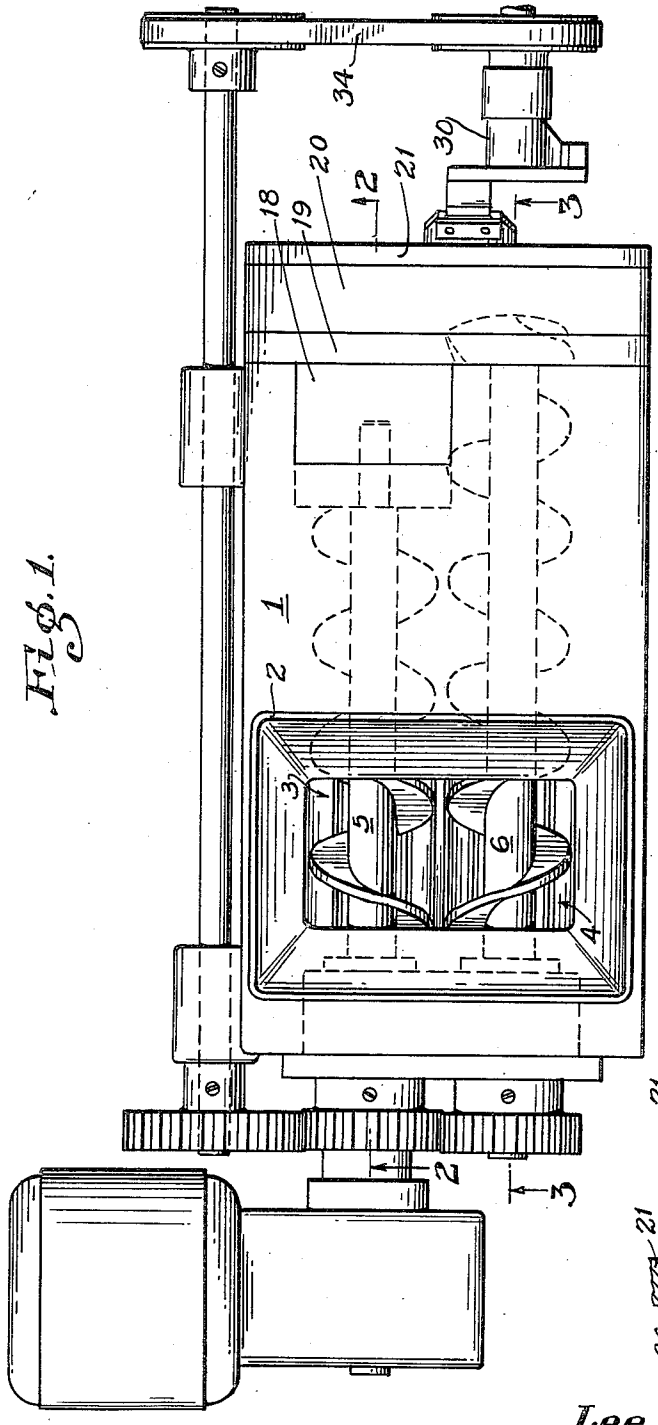


Fig. 1.

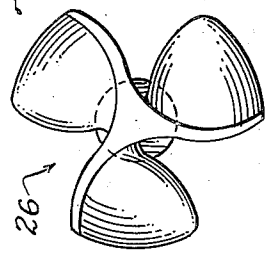


Fig. 8.

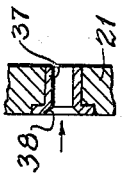


Fig. 12.

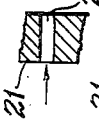


Fig. 9.

Fig. 10.

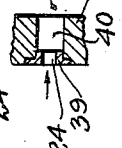


Fig. 14.

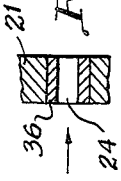


Fig. 11.

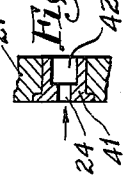


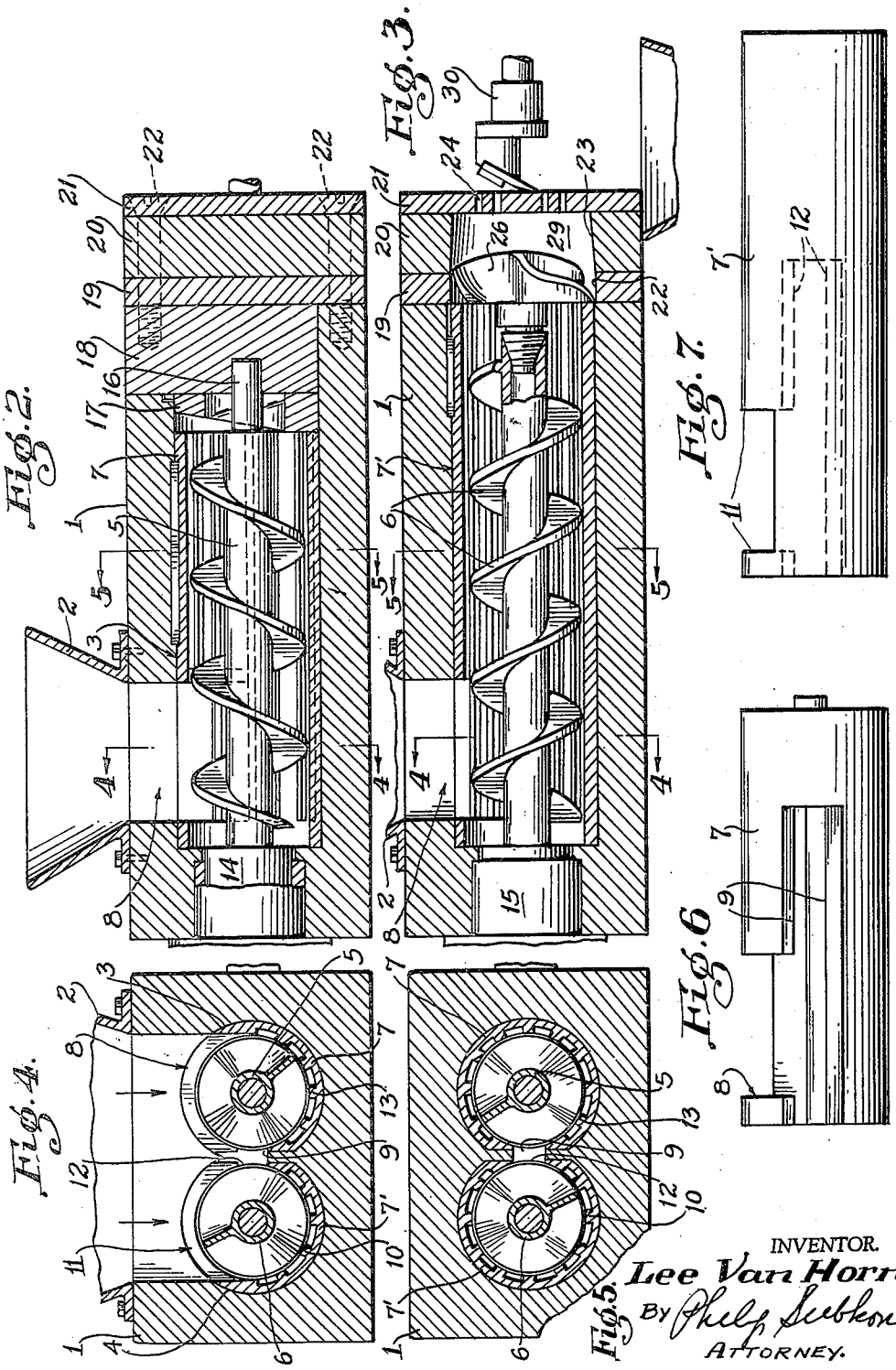
Fig. 13.

INVENTOR.
Lee Van Horn
BY Philip Lubkow
ATTORNEY.

Dec. 18, 1945. L. V. HORN 2,391,050

PROCESS FOR EXTRUDING ACID-ACTIVATED MONTMORILLONITE CLAY

Filed Jan. 25, 1944 2 Sheets-Sheet 2



INVENTOR.
Lee Van Horn
BY Philip Seibkow
ATTORNEY.

Patented Dec. 18, 1945 2,391,050

UNITED STATES PATENT OFFICE

2,391,050

PROCESS FOR EXTRUDING ACID-ACTIVATED MONTMORILLONITE CLAY

Lee Van Horn, West Los Angeles, Calif., assignor to Filtrol Corporation, Los Angeles, Calif., a corporation of Delaware

Application January 25, 1944, Serial No. 519,685

2 Claims. (Cl. 252—259.2)

This invention relates to a process and apparatus for the production of catalytically active, pelleted clay material.

Commercially among the most important of catalysts are the acid activated montmorillonite clay catalysts now widely used in processes of hydrocarbon conversion. These clays have also found great utility in other types of catalysis and as liquid and vapor adsorbents. In many of these processes it is desirable to form the clay into compact shapes, and one of the most convenient of methods for producing such shapes is by means of an extrusion press wherein the comminuted activated clays are extruded through a die plate containing orifices of desired shape, as, for instance, cylindrical orifices. In producing pellets by this method the clay is forced by means of a screw operating in a barrel through die holes in a die plate.

It has been found desirable in pelleted catalysts of this nature to hold the density of the pellet below an upper limit and to form a pellet of high mechanical rigidity and resistance to fracture and abrasion.

The mechanical strength and the density of the catalytic pellet thus formed depend on the character and nature of the compacting pressure which is generated by the screw in forcing the clay to and through the die plate. It has been observed that the density of the pellet is increased as the resistance to extrusion is increased. The capacity of an extrusion press increases as the speed of the press increases and this results in an increase in the power input to the press. As this is increased, the compacting pressure on the clay forced through the die orifice increases. This results in an increase in the density of the pellet.

These considerations impose a limitation either on the capacity of the extrusion press or upon the densities which may be obtained. Thus, for any given press, I may increase the capacity by increasing the speed of the screw. This increases the power input to the screw and results in an augmented compression of the clay and an increase in density of the pellet. I may produce a pellet of lower density by decreasing the power input, that is, the speed of the screw, but I will reduce the output of the press.

One of the important factors in controlling the power input necessary for a given capacity in such an extrusion operation is the frictional resistance of the pellet passing through the die hole. I have found that if this frictional resistance is diminished I may increase the throughput of clay through the press without increasing the compacting force to an undesirably high figure and therefore obtain a pellet at the higher production rates which will have the required density. The frictional resistance of the pellet through the die hole is the sliding resistance of the clay pellet over the metallic surface of the die orifice. This sliding resistance depends both on the chemical composition of the metal of the die orifice and on the characteristic of the surface of this die orifice. I have found that it is beneficial if the surface be a polished surface, for example, a mirror surface, in order that the frictional resistance be low for the purposes of this operation. Additionally, if the metal has a relatively low coefficient friction vis-à-vis the clay pellet, the resistance to the extrusion is further reduced.

The acid activated clays which are pelleted according to my invention are of themselves of acidic properties, being hydrogen montmorillonites.

Clays are activated commercially by treating with dilute acid for a period of time necessary to remove the desired amount of alumina from the clay. The process comprises contacting a sub-bentonite clay of the montmorillonite family with dilute sulfuric acid at concentrations from about 5% to 60%, for instance, about 15%, and employing acids in the amount of from 20 to 150 pounds of sulfuric acid (calculated as anhydrous) per 100 pounds of clay (calculated as volatile free), for instance, 30 pounds of H_2SO_4 per 100 pounds of clay. The temperature of the reaction is about 200° to 215° F. The time about six hours. This is sufficient to produce a clay having an Al_2O_3 content of from about 10% to 20%, for example, about 17%. The degree of extraction depends upon the activity desired and the use to which the clay is placed. The clay is then washed with water and separated from the acid by a series of decantation and washing steps in thickeners and settlers and finally filtered. The filtered clay is then dried to a moisture content of from 15% to 30% and ground to desired mesh size.

The clay has an acidity resulting from adsorbed sulfuric acid and aluminum sulfate. This acidity is determined by the so-called "boil-out" test, in which 5 grams of the clay are boiled with 50 cubic centimeters of distilled water, filtered, and the filter cake washed with 50 cubic centimeters of hot distilled water. The acidity is determined by titration, using phenolphthalein indicator. The acidity expressed in milligrams of KOH per gram of sample is termed "titratable" acidity.

Clays produced by the above procedure will contain an amount of acid varying from about 3

to 20 milligrams of KOH per gram of clay (i. e., a titratable acidity of 3 to 20), depending upon the amount of washing to which the clay has been exposed in the activation process.

As usually produced, clays will have a titratable acidity of from 2 or less to about 6 milligrams of KOH. However, for many oils, clays of titratable acidity of from 6 to 20 milligrams of KOH are to be preferred. Such clays appear to exhibit higher adsorptive powers, requiring less clay to give a desired oil decolorization than does a clay of from 2 to 4 milligrams of KOH titratable acidity. The titratable acidity of the clay depends on the extent of washing employed, and by regulating the washing, clays of titratable acidity from 0 to 20 or 30 milligrams of KOH per gram of clay may be obtained.

The clay is then mixed with the necessary water to bring the clay to the required moisture content for extrusion. This may range from 40% to 50%, and for best results on the above clays, in the range of 45% to 47% moisture. The clay is well mixed and passed to the extruder.

I have found that in pelleting clays of this character the metallic surfaces of the die orifice become pitted and corroded very rapidly so that the surface becomes rough. A polished orifice in a steel plate will rapidly become pitted and corroded.

This corrosion also introduces a second disadvantage and limitation on the process. The extrusion of the pellet through the die orifice adds a wiping action, i. e., erosion, to the corrosive action resulting from the chemical constitution of the clay. A rapid wear of the die orifice and an enlargement of its diameter results. For most catalytic purposes it is desired to maintain the diameter of the pellet uniform within relatively close tolerances. The enlargement of the diameter resulting from the action of corrosion and erosion necessitates frequent changes of the die plate in order to maintain the pellets true to gauge. In the extrusion operation the pellets are forced through the die plate and emerged from the other side of the die plate. They are then cut off by a knife. The pressure of the knife against the extruded pellet creates a pressure of the pellet against one side of the die orifice, resulting in a greater wear on that side. The result of this operation is that the die orifice does not wear uniformly circumferentially, resulting in a generally egg-shaped, enlarged orifice.

When such a condition obtains, the knife in cutting off the extruded pellet causes a flexing of the following material in the die orifice. This flexing of the material imposes strains which largely impair the mechanical strength of the pellet. The hardness of the pellet is most important when such pellets are used in modern hydrocarbon catalytic processes, such as in the catalytic cracking of petroleum. In such processes the pellets are formed into large beds. In some processes these beds are moving beds. The pellets are subjected to compression, resulting from the load of the bed, and to abrasion due to the movement of the bed and the movement of the pellets to and through catalytic and regeneration zones. The forces of abrasion and compression require that the pellets have considerable mechanical strength, and it is therefore important to obviate the difficulties resulting from the extrusion of the pellet through out-of-round holes, as previously described.

I have discovered that these difficulties can be obviated so as to produce pellets of desirable density and hardness without sacrificing extruder capacity by the use of a metal for the die orifice which can be given a high mirror-polish, which has a low inherent frictional resistance to the extrusion of the pellet and which has a high resistance to corrosion by the acidic components of the pellet, and which will retain its mirror-polish through the extrusion. As a result of using such a metal I may obtain an increased throughput without deleteriously increasing the density of the pellet and obtain uniform pellets of excellent mechanical strength.

I have found that nickeliferous alloys will take the high polish which I have found desirable and will resist corrosion and erosion of the clay and will maintain for prolonged periods their gauge and roundness and will permit the extrusion of uniform pellets of high rate which will have the desired density and hardness. Nickeliferous alloys which I have found useful include nickel chromium alloys, for instance, one having the following composition: nickel 79.5%; chromium 13%; iron 6.5%; manganese 0.25%; silicon 0.25%; copper 0.2%; carbon 0.08%; Monel metals (natural nickel and copper alloy) ranging in nickel from 65 to 67% and copper from 29 to 30%; for example, Monel metals, indicated as *a–e*, having the following composition:

	Ni	Cu	Fe	Si	Mn	C	Al
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
(*a*)	67	30	1.5	1.25	0.25	0.2	----
(*b*)	66	29	1.5	3	0.3	0.2	----
(*c*)	66	29	0.9	0.25	0.4	0.15	2.75
(*d*)	65	29	2	4	0.3	0.2	----
(*e*)	67	30	1.4	----	1.0	----	----

Ferrous alloys containing from about 14 to about 35% nickel and from 7 to 26% chromium may also be used, for example:

	Ni	Cr	Mo	Cu	C
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
(*f*)	14	16–18	2–3	----	.10
(*g*)	19–23	7–10	----	1–1.5	.25
(*h*)	33–36	14–16	----	----	.25
(*i*)	24–26	19–21	----	----	.25
(*j*)	22	19	3.5	----	0.07

High nickel ferrous alloys may also be used, for example:

(*k*) 10–18% Fe; 65–68% Ni; 17–19% Cr; 0.50% C; 1.07% Mn.
(*l*) 25% Fe; 60% Ni; 15% Cr.

The Monel metals are particularly useful for this purpose. I have found that this metal will retain its mirror polish during the extrusion process and will not be corroded or eroded to a material extent. The material also has a relatively low coefficient friction to the sliding of the acid activated clay pellet through the die orifice, resulting in a relatively low extrusion pressure at relatively high rates of extrusion. The resistance to erosion and corrosion of this material by the activated clay permits also of the production of pellets true to gauge. The pellets are extruded without any substantial flexure in the die orifice. As a result of the use of this material in my extrusion process and apparatus I am enabled to extrude acid treated clay at a high rate with a low extrusion pressure, thus producing a pellet of desirable density at a desirable extrusion rate. As a result of the resistance to corrosion the pellets in my process of extrusion are extruded through an orifice without any substantial flexure of the pellet in the orifice as the pellet is cut

off. I therefore produce by my process a substantially unflexed pellet of great mechanical strength.

This invention will be better understood by reference to the accompanying drawings wherein:

Fig. 1 is a plan view of the extruder;

Fig. 2 is a vertical section taken along the line 2—2 of Fig. 1;

Fig. 3 is a vertical section taken across line 3—3 of Fig. 1;

Fig. 4 is a transverse section taken along line 4—4 of Figs. 2 and 3;

Fig. 5 is a transverse section taken along 5—5 of Figs. 2 and 3;

Fig. 6 is an elevation of the liner 7;

Fig. 7 is a vertical elevation of the liner 7';

Fig. 8 is an end view of the impeller 26; and

Figs. 9, 10, 11, 12, 13, and 14 are details of the various orifices which may be employed in the die plate.

The extruder 1 carries a hopper 2 which feeds material to be extruded into barrels 3 and 4 in which barrels rotate the screws or augers 5 and 6. In barrel 3 is positioned a liner 7 having an opening 8 which registers with the opening of a hopper 2. Liner 7 also is cut away to provide a horizontal slot 9. In the barrel 4 is positioned a liner 7' having a slot 11 registering with the opening of a hopper 2 and a horizontal slot 12. These liners are so positioned that the slots 8 and 11 permit of the unobstructed entrance of the material to be extruded from the hopper 2 into the barrels 3 and 4. The slots 9 and 12 are positioned in registry with each other (see Figs. 3 and 4) to permit the easy passage of the material from barrel 3 into barrel 4. These liners may carry horizontal flutes, running the length of the barrel, formed by upstanding ribs 10 and 13, as will be later more fully described.

In barrel 3 is rotatably positioned an auger or screw 5 journalled at 14 at one end of the barrel and by means of the stub shaft 16 and plow 17 and block 18 at the other end of the barrel. In barrel 4 is rotatably positioned a screw or auger 6 journalled at one end at 15 and terminating at the other end 25 in a removable impeller 26 having a conical head 28 and vanes 27 (Fig. 8).

The barrel 3 is closed by a head 17 and a block 18, spacers 19 and 20 and die plate 21 held in place by screws 22. The spacer 19 is solid opposite the barrel 3 but is formed with a hole 22 through which the impeller 26 passes. The spacer 20 is formed with a tapered hole 23 to form a chamber 29. The die plate 22 carries perforations only at the chamber 29. These perforations are die orifices and are uniformly disposed across the die plate 24 at said chamber 29.

The liners 7 and 7' are preferably formed of the nickeliferous metals previously referred to and particularly of Monel. The screws 5 and 6 may likewise be made of such metal, as may the spacers 19, 20, and the die plate 21, or in the alternative these elements may be faced with such metal. However, the main portions of the extruder may be made of steel employing the nickeliferous metal liners and the die plates, as described herein.

Since the movement of acid treated clay through the barrel creates a large erosive effect at this point, I have found it desirable to have the surface in contact with the clay, especially where a rubbing action occurs, composed of the nickeliferous material previously referred to. However, in using this material, the property which I have found highly desirable in the orifice imposes a difficulty when employed in the barrel. The low frictional resistance to the sliding of the clay over such surfaces causes the clay in the extruder barrel to be merely rotated in place without being urged forward by the screw. For proper functioning of the screw type extruder the clay at the barrel surface should have a high frictional resistance to rotation while having a relatively lower frictional resistance with the surface of the screw, that is, the clay should be gripped at the barrel surface and slide over the face of the screw. In this fashion the screw has a wedge action to force the material forward. Thus, because of the lower sliding resistance of clay over Monel surfaces, the use of Monel at the screw is advantageous not only because of the resistance to corrosion and erosion at the screw surface but also because low frictional resistance assists the functioning of the screw to urge the material forward.

In order to overcome the low frictional resistance of this material at the Monel surfaces of the barrel, I have roughened this surface. This may be done by scoring, knurling, or otherwise indenting the surface. This may be accomplished by casting horizontal ribs shown at 10 and 13, Fig. 5, running longitudinally of the barrel. These ribs forming the flute or chamfer need be but of small dimensions. Thus, for instance, in a Monel metal barrel of 6" diameter, these ribs may be $\frac{5}{16}$" wide and $\frac{3}{16}$" high and spaced 1.57" on centers around the circumference of the barrel. This is sufficient to give the roughening of the surface necessary to overcome the low frictional resistance in the nickeliferous material employed.

The impeller 26 may also be either made of or surfaced with Monel metal or other nickeliferous alloy. The orifice plate may be formed of nickeliferous alloy such as Monel metal or may be made of steel with inserts of this metal as shown in Figs. 9 to 14, inclusive. In these figures the arrow indicates the direction of travel of the pellet being extruded.

Fig. 9 shows an orifice 24 of uniform cylindrical character formed in a Monel metal or other nickeliferous alloy die plate 21. Instead of forming the orifice of uniform diameter it may be chamfered to give a conical entrance to the orifice. One of the advantages of this enlargement of the die orifice at the entrance (see Fig. 10) is to break up the laminations of clay laid down by the auger against the die plate. Instead of employing the forms shown in Figs. 9 and 10, I may form the die plate of steel, but introduce a cylindrical insert 36 having a die orifice 24. This insert is formed of nickeliferous material such as Monel metal. The insert may be held in place either frictionally or by means of welding it in place. The orifice may be formed with a chamfered entrance as shown in Fig. 12. In that case the insert 37 carries a conical bevel 38. The orifice shown in Fig. 13 is formed with an insert 41 of nickeliferous alloy such as Monel metal in the steel die plate 21 carrying a counterbore 42 of diameter larger than die orifice 24. Such an orifice has the advantage of reduced frictional resistance to extrusion of the pellet. The die orifice is shorter in length than the thickness of the plate and therefore would have a smaller resistance to extrusion than the corresponding orifice of Fig. 11. However, such an orifice has the disadvantage that the pellet in the counterbore 42 is not gripped by the sides of the orifice in the

counterbore, and it may flex as a result of impact of the knife 30 operating against the face of the orifice plate of which the counterbore is formed. The form Fig. 14 shows an orifice similar to that of Fig. 13 formed by an insert 39 of nickeliferous metal, such as Monel, and carrying a bore 24 which is thus equivalent to the opening 24 of Fig. 13. The orifice 40 which is equivalent to counterbore 42 of Fig. 13 need not be made of nickeliferous alloy, since the clay does not rub against the sides of the orifice plate in the chamber 40 in the same way that it does in the opening 24.

These orifice inserts shown in Figs. 11, 12, 13, and 14 are held in such fashion as to be replaceable should the orifices wear beyond the gauge tolerances which are permitted. This may be done by loosening these inserts and dislodging them from position in the orifice plate and inserting new orifices. In this way the holes may be re-established without requiring a whole new plate.

While I have described a particular embodiment of my invention for the purpose of illustration, it should be understood that various modifications and adaptions thereof may be made within the spirit of the invention as set forth in the appended claims.

I claim:

1. A process for extruding an acid activated montmorillonite clay, which comprises forcing acid activated montmorillonite clay, containing enough water for extrusion, through a die orifice whose surface in contact with the clay being extruded is composed of Monel metal having a high wear resistance and a low frictional resistance to the motion of said clay through said die orifice and a high corrosion resistance to said acid activated clay, and correlating therewith the rate of extrusion and water content of the clay being extruded to produce catalyst pellets of satisfactory catalytic activity.

2. A process for producing extruded acid activated montmorillonite clay, which comprises extruding an acid activated montmorillonite clay containing from 40 to 50% water through a die orifice whose surface is composed of Monel metal, regulating the rate of extrusion of said clay through said die orifice so that at said rate of extrusion through said die orifice the extruded clay product will have physical characteristics suitable for cracking catalyst.

LEE VAN HORN.