United States Patent Office 3,255,102
Patented June 7, 1966

3,255,102

CATALYTIC CRACKING OF A POISONED FEEDSTOCK

Robert A. Sanford, Homewood, Ill., and Earl C. Gossett, Hammond, Ind., assignors to Sinclair Research, Inc., Wilmington, Del., a corporation of Delaware

No Drawing. Filed Mar. 16, 1962, Ser. No. 180,337
The portion of the term of the patent subsequent to Feb. 24, 1981, has been disclaimed
10 Claims. (Cl. 208—120)

This invention is a method for catalytically cracking hydrocarbon feedstocks containing metal contaminants which include demetallization of the catalyst when the poisoning metal reaches a high level.

One of the most important phases of study in the improvement of catalyst performance in hydrocarbon conversion is in the area of metals poisoning. Although referred to as "metals," these catalyst contaminants may be in the form of free metals or relatively non-volatile metal compounds. It is to be understood that the term "metal" used herein refers to either form. Various petroleum stocks have been known to contain at least traces of many metals. For example, Middle Eastern crudes contain relatively high amounts of several metal components, while Venezuelan crudes are noteworthy for their vanadium content and are relatively low in other contaminating metals such as nickel. In addition to metals naturally present, including some iron, petroleum stocks have a tendency to pick up tramp iron from transportation, storage and processing equipment. Because most of these metals, when present in a stock, deposit in a relatively non-volatile form on the catalyst during the conversion processes and regeneration of the catalyst to remove coke does not remove these contaminants, such feeds are generally avoided in conventional processing.

Cracking of heavier hydrocarbon feedstocks to produce hydrocarbons of preferred octane rating boiling in the gasoline range is widely practiced and is ordinarily effected to produce gasoline as the most valuable product and is generally conducted at temperatures of about 750 to 1100° F., preferably about 850 to 950° F., at pressures up to about 200 p.s.i.g., preferably about atmospheric to 100 p.s.i.g., and without substantial addition of free hydrogen to the system. In cracking, the feedstock is usually a mineral oil or petroleum hydrocarbon fraction such as straight run or recycle gas oils or other normally liquid hydrocarbons boiling above the gasoline range.

Solid oxide catalysts have long been recognized as useful in catalytically promoting conversion of hydrocarbons. For cracking processes, the catalysts which have received the widest acceptance today are usually activated or calcined predominantly silica or silica-based, e.g., silica-magnesia, silica-zirconia, silica-alumina, etc., compositions in a state of slight hydration and containing small amounts of acidic oxide promoters in many instances. These oxides may also contain small amounts of other inorganic materials, but current practice in catalytic cracking leans more toward the exclusion from the silica materials of foreign constituents such as alkaline metal salts which may cause sintering of the catalyst surface on regeneration and a drop in catalytic activity. For this reason, the use of wholly or partially synthetic gel catalysts, which are more uniform and less damaged by high temperatures in treatment and regeneration, is often preferable. Most of the catalysts, however, which are used in conventional cracking processes are very sensitive to metals. Iron, nickel, vanadium and copper, for example, markedly alter the selectivity and activity of conventional cracking reactions if allowed to accumulate, producing a higher yield of coke and hydrogen at

the expense of desired products, such as gasoline and butanes. For instance, it has been shown that the yield of butanes, butylenes and gasoline, based on converting 60 volume percent of cracking feed to lighter materials and coke dropped from 58.5 to 49.6 vol. percent when the amount of nickel on the conventional catalyst employed increased from 55 p.p.m. to 645 p.p.m. and the amount of vanadium increased from 145 p.p.m. to 1480 p.p.m. in a more or less conventional catalytic cracking of a normally liquid feed stock containing some metal contaminated stocks. Since many cracking units are limited by coke burning or gas handling facilities, increased coke or gas yields require a reduction in conversion or throughput to stay within the unit capacity.

Refiners cope with the problem of metal poisoning by adopting several techniques. One technique includes selecting only feedstocks of low metal content or treating the feedstock to minimize its metal content. Another technique requires removing from the hydrocarbon conversion system as much metal as is fed to it per unit time, in order to obtain and retain a total amount of metal in the system below a level where the conversion process is made economically unfeasible by the poisoning effect of the metal, which usually is proportional to the amount of metal on the catalyst. In most conversion processes some metal-containing catalyst is continually lost from the system in the form of fines which leave the system with effluent gases. The replacement of this loss with fresh unpoisoned catalyst reduces the net amount of metal in the system. In addition, the refiner usually will purposely remove enough poisoned catalyst from the system per unit time so that replacement with unpoisoned or less poisoned catalyst will keep the metal level at the desired equilibrium. The removed catalyst may be discarded as a waste material, or, using recently developed techniques, the catalyst may be demetallized and returned to the system.

The catalyst employed in this invention is more resistant to metals, especially nickel, than conventional cracking catalysts; that is, metals accumulation on the catalyst of this invention has less poisoning on the system. In operating with such a catalyst in this invention, the petroleum refiner allows more metal to accumulate on the catalyst than with a conventional catalyst, without severe, economically disadvantageous, effects on the product distribution. By allowing a greater metals accumulation, that is, by operating at a higher equilibrium metal level, the inevitable stack loss of catalyst fines allows removal of more metal from the system. Further, less catalyst needs to be demetallized to keep the proper conversion efficiency with a feedstock of given metal content.

This invention conducts a cracking operation using this particular type of cracking catalyst which is resistant to the poisoning effects of moderate levels of metal contaminants and which is demetallized when the metal levels become high. In the invention, the hydrocarbon petroleum oils utilized as feedstock for a conversion process may be of any desired type normally utilized in catalytic conversion operations but those stocks are generally used which are normally considered too highly contaminated with metal, especially nickel. In most cases the feedstock contains vanadium and perhaps other metals mentioned above. Sometimes as much as 5 to 25 parts per million of nickel and/or 5 to 50 parts per million vanadium may be in the feedstock and may result from blending a feedstock component containing perhaps as much as about 0.5% metal with a relatively unpoisoned stock. The process of this invention is especially useful in treating feedstock containing residual petroleum or heavy distil-

late components, that is, atmospheric tower bottoms and materials derived therefrom.

The catalyst may be used as a fixed, moving or fluidized bed or may be in a more dispersed state. For typical operations, the catalytic cracking of the hydrocarbon feed would normally result in a conversion of about 50–60 percent of the feedstock into a product boiling in the gasoline boiling range.

This invention employs a synthetic or semi-synthetic catalyst prepared by mixing with or coating with hydrous alumina, precipitated from an aqueous solution, a silica-alumina base or substrate.

The substrate is a solid inorganic oxide mixture, generally a clay or a synthetic silica gel. The substrate usually contains at least about 40% silica and often is predominantly silica. Preferably the substrate contains alumina, generally in an amount of at least about 5 to 30% and the combined silica and alumina content is at least about 85 or 90% of the substrate, the remainder, if any, generally comprising other inorganic oxides, such as those found originally in the clay, or added for additional promoting effects. The substrate may be derived from one of the clays conventionally used in catalytic cracking, such as halloysite or dehydrated halloysite (kaolinite) or bentonite. In most cases it is desirable to treat the clay with mineral acid for purposes of activation or at least for iron removal. The substrate may also be a completely synthetic-gel oxide material, which may be silica-based and ordinarily contains a substantial amount of a gel or gelatinous precipitate comprising a major portion of silica and at least one other material, such as alumina, magnesia, zirconia, etc.

The substrate is in the form of recognizable particles. While the size range of the particles is not of the utmost significance, the particles are greater than colloidal in size, that is, they are larger than the micelles, the submicrons particles which make up a colloid. The substrate particles may be characterized by their lack of electric charge and the fact that they do not disperse to form a colloid when placed in an aqueous medium, and even if severely agitated, do not form a true, stable, colloidal suspension but rather settle, on standing, to leave a supernatant liquid. Also, particles suitable for forming the substrate do not grow by accretion or inorganic polymerization with each other. The silica-based gel substrate is generally prepared for alumina deposition by being washed, dried, if desired, and sized. Although there usually is no need for calcination before alumina addition, this may be performed, and the substrate will usually exhibit cracking activity upon calcination.

Hydrated alumina gel is mixed with the substrate particles to form the catalyst. Alternatively the alumina gel can be prepared in the presence of the substrate particles. Preferably the hydrated gel is formed by reacting ammonia with an aqueous solution of an aluminum salt after which the alumina hydrate or alumina hydrate-substrate slurry is washed and the hydrate concentrated as by settling and the aqueous material filtered off. Precipitation of alumina from an aqueous solution of an alkali aluminate by addition of an acid may also be employed. Also, the hydrous alumina may be precipitated by hydrolysis from alcohol solutions of aluminum alkoxides, although the use of aluminum salts, generally a sulfate, such as $Al_2(SO_4)_3$ or $NH_4Al(SO_4)_2$ is preferred.

During the formation of the alumina hydrate the pH is generally controlled to produce certain characteristics in the alumina hydrate. For example, according to U.S. Patent 2,935,463, a steam resistant catalyst is formed when the precipitation is performed at a pH greater than 10. Also, when the catalyst is prepared by precipitation of hydrous alumina in the presence of the substrate, at a pH of about 5 to 9, the conditions serve to give a catalyst having the precipitated alumina substantially entirely in the amorphous form as determinable by standard monochromatic X-ray diffraction using a tungsten cathode.

This precipitation preferably takes place at a pH of about 7 to 7.5.

Generally 100 parts of substrate on a dry basis are used for each 3 to 100, preferably about 10 to 25 parts of alumina gel, also on a dry basis. Thus the finished catalyst contains about 3 to 50% of synthetic alumina precipitated on or mixed with the substrate, preferably about 9 to 20% and the total alumina content of the catalyst is between about 10 and 65 percent, preferably around 15 to 50% on a dry basis. For example, about 10 to 20 parts synthetic alumina hydrate gel may be precipitated on about 100 parts of an acid-treated clay containing about 20% alumina to give a catalyst having a total alumina (natural and synthetic) content of about 27 to 33%.

The solution from which alumina is precipitated may contain a concentration of about 5 to 20% of the aluminum salt and the substrate will often make up about 10 to 20%, of the total slurry weight. Ammonia, or more preferably ammonia water, or other aqueous base, can be added to the solution until the desired amount of alumina hydrate gel is precipitated. Preferably, at the end of precipitation, the slurry is so thick that it just barely can be stirred. The alumina hydrate-substrate slurry is washed and the hydrate concentrated as by setting, and the aqueous material is filtered off, after which the catalyst precursor is thoroughly washed to remove sulfate or other interfering anions.

The substrate particles will generally be provided in a fluidizable particle size and thus the resulting coated material will be fluidizable. Alternatively the coated substrate may be formed to macro-shape by pelleting, extrusion, etc., dried, and generally the catalyst is calcined before use.

The physical form of the catalyst varies with the type of manipulative process to which it will be exposed. In fluid processing, gases are used to convey the catalyst between reaction and regeneration zones and to keep it in the form of a dense turbulent bed which has no definite upper interface between the dense (solid) phase and the suspended (gaseous) phase mixture of catalyst and gas. This type of processing requires the catalyst to be in the form of a fine powder, generally in a size range of about 20 to 150 microns or less. Fixed and moving catalyst beds may also be employed and in such cases the catalyst is in micro particle size, e.g., about 1/16 to 1/2 inch in diameter and 1/16 to 1 inch in length. These dimensions are usually 1/8 to 1/4 inch. In the case of bead catalysts, the diameter may be of comparable size. Preferably this invention employs fluidized solids techniques.

A number of procedures have been developed for the removal of poisoning metals from catalysts conventionally used in cracking procedures. These demetallization operations are described, for example, in copending applications, Serial Nos. 758,681, filed September 3, 1958, now abandoned; 763,833 and 763,834, filed September 29, 1958, now abandoned; 767,794, filed October 17, 1958, now abandoned; 842,618, filed September 28, 1959, now abandoned; 849,199 filed October 28, 1959, now abandoned; 19,313, filed April 1, 1960, now abandoned; 39,810, filed June 30, 1960, now abandoned; 47,598, filed August 4, 1960, now U.S. Patent No. 3,168,482; 53,380, filed September 1, 1960, now U.S. Patent No. 3,122,497; 53,623, filed September 2, 1960, now abandoned; 54,368, now U.S. Patent No. 3,122,512; 54,405, now U.S. Patent No. 3,122,510; and 54.532, now abandoned, filed September 7, 1960; 55,129, now U.S. Patent No. 3,147,209; 55,160, now U.S. Patent No. 3,150,103 and 55,184, now abandoned, filed September 12, 1960; 55,703, filed September 13, 1960, now abandoned; 55,838, filed September 14, 1960, now abandoned; 67,518, filed November 7, 1960, now U.S. Patent No. 3,208,952; 73,199, filed December 2, 1960, now U.S. Patent No. 3,151,088; 81,256 and 81,257, filed January 9, 1961, now abandoned; 95,101, filed March 13, 1961, now aban-

doned; 115,617, filed June 8, 1961, now U.S. Patent No. 3,151,059, and 167,903 filed January 22, 1962 all of which are hereby incorporated by reference.

In these treatments to take poisoning metals from conventional cracking catalysts the amount of metal is removed which is necessary to keep the average metal content of the catalyst in the cracking system below the limit of the unit's tolerance for poison.

In the process of this invention, however, the tolerance of the unit for poisoning metal is considerably greater due to the special catalyst used. Such increased tolerance is of value in a number of respects as mentioned above. First, the greater amount of poisoning metal allowed to accumulate on the catalyst permits a greater amount of metal to be lost from the system with the lost fines. Further, the tolerance of the cracker for poison determines to a large extent the amount of metals removed in the catalyst demetallization procedure. Where the catalyst contains a greater amount of poisoning metal, a particular treatment will remove a greater amount of metal; for example, if the cracker can tolerate an average of 100 p.p.m. Ni and the demetallization process can remove 50% of the nickel content of the catalyst, only 50 p.p.m. of nickel can be removed in a pass through the catalyst demetallization system. However, where the cracker can tolerate 1500 p.p.m. of nickel, it is possible to remove 750 p.p.m. nickel from the catalyst with each pass through the demetallization system. Thus, although the catalysts used in this invention do not show a great improvement in cracking selectivity due to variations in metal content at moderate levels, that is, where demetallization is conducted on a catalyst containing less than about 800 p.p.m. nickel and/or 1000 p.p.m. vanadium (measured as the common oxides) removal of metal does not bring about a proportional increase in cracking effectiveness, when the unit is operated at a higher metals level demetallization brings about greater metals removal than commercially realizable with ordinary catalyst and such removal improves catalyst performance significantly. The tolerance of the unit for poisoning metal oxide is seldom greater than about 5000 to 10,000 p.p.m. and preferably the metals level is kept below about 2000 p.p.m. NiO and 2000 p.p.m. V_2O_5.

The cracking procedure of this invention generally includes a regeneration step for burning carbon off the catalyst. It will be understood that in this specification and claims "regeneration" refers to this carbon burn-off procedure. After regeneration, subjecting the poisoned catalyst sample to magnetic flux may be found desirable to remove any tramp iron particles which may have become mixed with the catalyst. Regeneration of a catalyst to remove carbon is a relatively quick procedure in most commercial catalytic conversion operations. For example, in a typical fluidized cracking unit, a portion of catalyst is continually being removed from the reactor and sent to the regenerator for contact with air at about 950 to 1300° F., more usually about 1000 to 1200° F. Combustion of coke from the catalyst is rapid, and for reasons of economy only enough air is used to supply the needed oxygen. Average residence time for a portion of catalyst in the regenerator may be of the order of about six minutes and the oxygen content of the effluent gases from the regenerator is desirably less than about ½%. The regeneration of any particular quantum of catalyst is generally regulated to give a carbon content of less than about 1.0%, generally less than about 0.5%. Regeneration puts the catalyst in a substantially carbon-free state, that is, the state where little, if any, carbon is burned or oxygen consumed even when the catalyst is contacted with oxygen at temperatures conductive to combustion.

In the treatment to take poisoning metals from the cracking catalyst a large or small amount of metal can be removed as desired. The demetallization treatment generally removes about 10 to 90% of one or more poisoning metals from a catalyst portion which passes through the treatment. Advantageously a demetallization system is used which removes about 60 to 90% nickel and 20 to 40% vanadium from the treated portion of catalyst. Preferably at least 50% of the equilibrium nickel content and 15% of the equilibrium vanadium content is removed. The actual time or extent of treating depends on various factors, and is controlled by the operator according to the situation he faces, e.g., the extent of metals content in the feed, the level of conversion unit tolerance for poison, the sensitivity of the particular catalyst toward a particular phase of the demetallization procedure, etc. Also, the thoroughness of treatment of any quantum of catalyst in commercial practice is balanced against the demetallization rate chosen; that is, the amount of catalyst, as compared to the total catalyst in the conversion system proper, which is subjected to the demetallization treatment per unit of time. A high rate of catalyst withdrawal from the conversion system and quick passage through a mild demetallization procedure may suffice as readily as a more intensive demetallization at a slower rate to keep the total of poisoning metal in the conversion reactor within the tolerance of the unit for poison. In a continuous operation of the commercial type a satisfactory treating rate may be about 5 to 50% of the total catalyst inventory in the system, per twenty-four-hour day of operation although other treating rates may be used. With a continuously circulating catalyst stream, such as in the ordinary "fluid" system a slip-stream of catalyst, at the "equilibrium" level of poisoning metals may be removed intermittently or continuously from the regenerator standpipe of the cracking system. The catalyst is subjected to one or more of the demetallization procedures described hereinafter and then the catalyst, substantially reduced in contaminating metal content, is returned to the cracking system.

The above-mentioned copending patent applications describe procedures by which poisoning metals included in a solid oxide hydrocarbon conversion catalyst are removed by dissolving them from the catalyst or subjecting the catalyst, outside the hydrocarbon conversion system, to elevated temperature conditions which put the metal contaminants into the chloride, sulfate or other volatile, water-dispersible or more available form. A significant advantage of these processes lies in the fact that the overall metals removal operation, even if repeated, does not unduly deleteriously affect the activity, selectivity, pore structure and other desirable characteristics of the catalyst.

Treatment of the regenerated catalyst with molecular oxygen-containing gas is employed to improve the removal of vanadium from the poisoned catalyst. This treatment is described in copending application Serial No. 19,313, filed April 1, 1960, and is preferably performed at a temperature at least about 50° F. higher than the regeneration temperature, that is, the average temperature at which the major portion of carbon is removed from the catalyst. The temperature of treatment with molecular oxygen-containing gas will generally be in the range of about 1000 to 1800° F. but below a temperature where the catalyst undergoes any substantial deleterious change in its physical or chemical characteristics, preferably a temperature of about 1150 to 1350° or even as high as 1600° F. The duration of the oxygen treatment and the amount of vanadium prepared by the treatment for subsequent removal is dependent upon the temperature and the characteristics of the equipment used. If any significant amount of carbon is present in the catalyst at the start of this high-temperature treatment, the essential oxygen contact is that continued after carbon removal, which may vary from the short time necessary to produce an observable effect in the later treatment, say, a quarter of an hour to a time just long enough not to damage the catalyst. In any event, after carbon removal, the oxygen treatment of the essentially carbon-free catalyst is at least long enough to stabilize a substantial

amount of vanadium in its highest valence state at the catalyst surface, as evidenced by a significant increase, say at least about 10%, preferably at least about 100%, in the vanadium removal in subsequent stages of the process. This increase is over and above that which would have been obtained by the other metals removal steps without the oxygen treatment. The maximum practical time of treatment will vary from about 4 to 24 hours, depending on the type of equipment used. The oxygen-containing gas used in the treatment contains molecular oxygen as the essential active ingredient and there is little significant consumption of oxygen in the treatment. The gas may be oxygen, or a mixture of oxygen with inert gas, such as air or oxygen-enriched air, containing at least about 1%, preferably at least about 10% O_2. The partial pressure of oxygen in the treating gas may range widely, for example, from about 0.1 to 30 atmospheres, but usually the total gas pressure will not exceed about 25 atmospheres.

The catalyst may pass directly from the oxygen treatment to a vanadium removal treatment especially where this is the only important contaminant. Such treatment may be a basic aqueous wash such as described in copending patent applications Serial No. 767,794 and Serial No. 39,810. Alternatively vanadium may be removed by a chlorination procedure as described in copending application Serial No. 849,199, although unpromoted chlorination and its auxiliary treatments as described in copending applications Serial Nos. 55,838 and 167,903 may work best where the catalyst is one which contains "natural" clay components. Vanadium may be removed from the catalyst after the high temperature treatment with molecular oxygen-containing gas by washing it with a basic aqueous solution. The pH is frequently greater than about 7.5 and preferably the solution contains ammonium ions which may be in the form of NH_4+ ions or organic-substituted NH_4+ ions such as methyl ammonium and quaternary hydrocarbon radical ammoniums. The amount of ammonium ion in the solution is sufficient to give the desired vanadium removal and will often be in the range of about 1 to 25 or more pounds per ton of catalyst treated. The temperature of the wash solution may vary within wide limits: room temperature or below, or higher. Temperatures above 215° F. require pressurized equipment, the cost of which does not appear to be justified. Very short contact times, for example, about a minute, are satisfactory, while the time of washing may last 2 to 5 hours or longer. After the ammonium wash the catalyst slurry can be filtered to give a cake which may be reslurried with water or rinsed in other ways, such as, for example, by a water wash on the filter, and the rinsing may be repeated, if desired, several times.

Alternatively, after the high temperature treatment with oxygen-containing gas, treatment of a metals contaminated catalyst with a chlorinating agent at a moderately elevated temperature up to about 1000° F. is of value in removing vanadium and iron contaminants from the catalyst as volatile chlorides. This treatment is described in copending applications Serial Nos. 849,199, 54,405, 54,532, 55,703, and 67,518. The chlorination takes place at a temperature of at least about 300° F. up to about 1000° F., preferably about 550 to 650° F. with optimum results usually being obtained near 600° F. The chlorinating agent is essentially anhydrous, that is, if changed to the liquid state no separate aqueous phase would be observed in the reagent.

The chlorinating reagent is a vapor which contains chlorine. When the catalyst is a completely synthetic gel material, HCl may sometimes be substituted for the chlorine. The chlorinating reagent preferably employs a carbon or sulfur compound. Thus the agent may be a mixture of chlorine with, for example, a chlorine substituted light hydrocarbon, such as carbon tetrachloride, which may be used as such or formed in-situ by the use of, for example, a vaporous mixture of chlorine gas with low molecular weight hydrocarbons such as methane, n-pentane, etc. About 1–10 percent active chlorinating agent based on the weight of the catalyst is generally used. The carbon or sulfur compound promoter is generally used in the amount of about 1–5 or 10 percent or more, preferably about 2–3 percent, based on the weight of the catalyst for good metals removal; however, even if less than this amount is used, a considerable improvement in metals conversion is obtained over that which is possible at the same temperature using chlorine alone. The chlorine and promoter may be supplied individually or as a mixture to a poisoned catalyst. Such a mixture may contain about 0.1 to 50 parts chlorine per part of promoter, preferably about 1–10 parts per part of promoter. A chlorinating gas comprising about 1–30 weight percent chlorine, based on the catalyst, together with one percent or more S_2Cl_2 gives good results. Preferably, such a gas provides 1–10 percent Cl_2 and about 1.5 percent S_2Cl_2, based on the catalyst. A "saturated" mixture of CCl_4 and Cl_2 or HCl can be made by bubbling chlorine or hydrogen chloride gas at room temperature through a vessel containing CCl_4; such a mixture generally contains about 1 part CCl_4/5–10 parts Cl_2 or HCl. Conveniently, a pressure of about 0–100 or more p.s.i.g., preferably about 0–15 p.s.i.g. may be maintained in chlorination. The chlorination may take about 5 to 120 minutes, more usually about 20 to 60 minutes, but shorter or longer reaction periods may be possible or needed, for instance, depending on the linear velocity of the chlorinating and purging vapors.

The demetallization procedure employed in this invention may be directed toward nickel removal from the catalyst, generally in conjunction with vanadium removal. Nickel may be removed directly from the catalyst by dissolving the nickel compounds or converting them to volatile materials such as nickel carbonyl and/or materials removable by an aqueous medium, e.g., water or dilute acid. The water removable form may be one which decomposes in water to produce water-soluble products. The removal procedure for the converted metal may be based on the form to which the metal is converted. The mechanism of the washing steps may be one of simultaneous conversion of nickel and/or vanadium to removable form and removal by the aqueous wash; however, this invention is not to be limited by such a theory.

Conversion of some of the metal poisons, especially nickel, to the sulfate form, as described in copending application Serial No. 758,681, comprises subjecting the catalyst to a sulfating gas, that is SO_2, SO_3 or a mixture of SO_2 and O_2, at an elevated temperature. Sulfur oxide contact is usually performed at a temperature of about 500 to 1200° F. and frequently it is advantageous to include some free oxygen in the treating gas. Another procedure, described in copending applications Serial Nos. 763,834 and 842,618, includes sulfiding the catalyst and performing an oxidation process, after which metal contaminants, preferably prior to an ammonium wash, may be removed from the catalyst by an aqueous medium.

The sulfiding step can be performed by contacting the poisoned catalyst with elemental sulfur vapors, or more conveniently by contacting the poisoned catalyst with a volatile sulfide, such as H_2S, CS_2 or a mercaptan. The contact with the sulfur-containing vapor can be performed at an elevated temperature, generally in the range of about 500 to 1500° F., preferably about 800 to 1300° F. Other treating conditions can include a sulfur-containing vapor partial pressure of about 0.1 to 30 atmospheres or more, preferably about 0.5 to 25 atmospheres. Hydrogen sulfide is the preferred sulfiding agent. Pressures below atmospheric can be obtained either by using a partial vacuum or by diluting the vapor with gas such as nitrogen or hydrogen. The time of contact may vary on the basis of the temperature and pressure chosen and other factors such as the amount of metal to be

removed. The sulfiding may run for, say up to about 20 hours or more depending on these conditions and the severity of the poisoning. Temperatures of about 900 to 1200° F. and pressures approximating 1 atmosphere or less seem near optimum for sulfiding and this treatment often continues for at least 1 or 2 hours but the time, of course, can depend upon the manner of contacting the catalyst and sulfiding agent and the nature of the treating system, e.g., batch or continuous, as well as the rate of diffusion within the catalyst matrix. The sulfiding step performs the function not only of supplying a sulfur-containing metal compound easily susceptible to removal in later steps but appears to concentrate some metal poisons, notably nickel, at the surface of the catalyst. In addition, oxidation after sulfiding may be performed by a gaseous oxidizing agent to provide metal poisons in a dispersible form. Gaseous oxygen, or mixtures of gaseous oxygen with inert gases such as nitrogen, may be brought into contact with the sulfided catalyst at an oxygen partial pressure of about 0.2 atmosphere and upward, temperatures upward of room temperature and usually not above about 1300° F., and times dependent on temperature and oxygen partial pressure. Gaseous oxidation is best carried out near 900° F., about one atmosphere O_2 and at very brief contact times.

The metal sulfide may be rendered water-dispersible by a liquid aqueous oxidizing agent such as a dilute hydrogen peroxide or hypochlorous acid water solution, as described in copending application Serial No. 842,618, filed September 28, 1959. The inclusion in the liquid aqueous oxidizing solution of sulfuric acid or nitric acid has been found greatly to reduce the consumption of peroxide. In addition the inclusion of nitric acid in the oxidizing solution provides for increased vanadium removal. Useful proportions of acid to peroxide to catalyst generally include about 2 to 25 pounds acid (on a 100% basis) to about 1 to 30 pounds or more H_2O_2 (also on a 100% basis) in a very dilute aqueous solution, to about one ton of catalyst. A 30% H_2O_2 solution in water seems to be an advantageous raw material for preparing the aqueous oxidizing solution. Sodium peroxide or potassium peroxide may be used in place of hydrogen peroxide and in such circumstances, extra sulfuric or nitric acid may be used.

Another highly advantageous oxidizing medium is an aerated dilute nitric acid solution in water. Such a solution may be provided by continuously bubbling air into a slurry of the catalyst in very dilute nitric acid. Other oxygen-containing gases may be substituted for air. Varying oxygen partial pressure in the range of about 0.2 to 1.0 atmosphere appears to have no effect in time required for oxidation, which is generally at least about 7 to 8 minutes. The oxidizing slurry may contain about 20% solids and provide about five pounds of nitric acid per ton of catalyst. Studies have shown a greater concentration of HNO_3 to be of no significant advantage. Other oxidizing agents, such as chromic acid where a small residual Cr_2O_3 content in the catalyst is not significant, and similar aqueous oxidizing solutions such as water solutions of manganates and permanganates, chlorites, chlorates and perchlorates, bromites, bromates and perbromates, iodites, iodates and periodates, are also useful. Bromine or iodine water, or aerated, ozonated or oxygenated water, with or without acid, also will provide a dispersible form. The conditions of oxidation can be selected as desired. The temperature can conveniently range up to about 220° F. with temperatures of above about 150° F. being preferred. Temperatures above about 220° F. necessitate the use of superatmospheric pressures and no need for such has been found.

After provision of nickel in a dispersible form, the catalyst is washed with an aqueous medium to remove the metal compound. This aqueous medium, for best removal of nickel, is generally somewhat acidic, and this condition may be brought about, at least initially, by the presence of an acid-acting salt or some entrained acidic oxidizing agent on the catalyst. The aqueous medium can contain extraneous ingredients in trace amounts, so long as the medium is essentially water and the extraneous ingredients do not interfere with demetallization or adversely affect the properties of the catalyst. Ambient temperatures can be used in the wash but temperatures of about 150° F. to the boiling point of water are sometimes helpful. Pressures above atmospheric may be used but the results usually do not justify the additional equipment. Where an aqueous oxidizing solution is used, the solution may perform part or all of the metal compound removal simultaneously with the oxidation. In order to avoid undue solution of alumina from a chlorinated catalyst, contact time in this stage is preferably held to about 3 to 5 minutes which is sufficient for nickel removal. Also, since a slightly acidic solution is desirable for nickel removal, this wash preferably takes place before the ammonium wash.

Alternative to the removal of poisoning metals by procedures involving contact of the sulfided or sulfated catalyst with aqueous media, nickel poison and some iron may be removed through conversion of the nickel sulfide to the volatile nickel carbonyl by treatment with carbon monoxide, as described in copending application Serial No. 47,598. In such procedures the catalyst is treated with hydrogen at an elevated temperature during which nickel contaminant is reduced to the elemental state, then treated, preferably under elevated pressure and at a lower temperature with carbon monoxide, during which nickel carbonyl is formed and flushed off the catalyst surface. Hydrogenation takes place at a temperature of about 800 to 1600° F., at a pressure from atmospheric or less up to about 1000 p.s.i.g. with a vapor containing 10 to 100% hydrogen. Preferred conditions are a pressure up to about 15 p.s.i.g. and a temperature of about 1100 to 1300° F. and a hydrogen content greater than about 80 mole percent. The hydrogenation is continued until surface accumulations of poisoning metals, particularly nickel, are substantially reduced to the elemental state. Carbonylation takes place at a temperature substantially lower than the hydrogenation, from about ambient temperature to 300° F. maximum and at a pressure up to about 2000 p.s.i.g., with a gas containing about 50–100 mole percent CO. Preferred conditions include greater than about 90 mole percent CO, a pressure of up to about 800 p.s.i.g. and a temperature of about 100–180° F. The CO treatment serves generally both to convert the elemental metals, especially nickel and iron, to volatile carbonyls and to remove the carbonyl.

Preferably, the treatment of the metal poison resistant catalysts used in this invention comprises removal from the hydrocarbon conversion system, sulfidation, unpromoted chlorination and a particular aqueous wash for metal removal. Sulfiding and chlorination are performed as described above, but usually elemental chlorine alone is used as the chlorinating agent and there is substantially no formation of volatile chlorides in the step. This chlorination, particularly when conducted in the lower temperature ranges, e.g., below about 550° F. is effective for conversion of nickel to nickel chloride and for conversion of iron and vanadium to forms, probably non-volatile chlorides, removable in the later wash. The contact with molecular chlorine may be at atmospheric pressure, or below or above. Subatmospheric pressures may be achieved by the use of vacuum or preferably by dilution with inert gas such as nitrogen or flue gas. Generally at whatever pressure is used, at least about 0.5 or 1 weight percent chlorine based on the catalyst is employed. The upper limit is based on economics; no reason has been found to use more than about 10% chlorine, but 25% or more could be used. The time of contact, of course, depends on the amount of chlorine supplied per unit time and is sufficient to give conversion of substantial nickel to nickel chloride and to substantially improve the

effect of the wash on other poisoning metals. 15 minutes to 2 hours is a practical time range but the chlorination may be accomplished in 5 minutes or may take 5 or more hours.

After such chlorination poisoning metal is removed from the catalyst by dissolving the metal in an aqueous medium. The exact nature of this medium may sometimes vary with the results desired and with the preliminary treatments given the catalyst. The aqueous medium may be provided with peroxy ions, or with a chelating agent or the catalyst may be treated with a reducing agent before, or simultaneously with the aqueous wash. Chelating or reducing agents or peroxide in the aqueous medium are used in amounts sufficient to give the desired removal of available metals from the catalyst, say at least about 0.1% agent based on the catalyst weight, in solution in tap water or distilled or deionized water. The upper limit on the reagent is generally determined by economic factors. Rarely would more than about 10% be used. The preferred amount is about 0.2 to 5%, Slurry concentrations from about 5 to 40% solids can be used with convenience in the washing step. The washing temperature can, for example, be 40 to 200° F. but preferably is about room temperature, that is, about 60 to 100° F. The slurry of catalyst in the aqueous medium may be brought to this temperature by the heat imparted to the solution by the hot catalyst following its preliminary vapor treatment. During the washing the catalyst should be stirred enough so that it is suspended in the solution.

If a chelating agent is employed, it preferably is an organic carboxylic acid. Aqueous solutions containing cyanide or hexameta phosphate ions are useful in forming soluble complexes with the poisoning metals. However, organic sequestering agents are preferred, since they form soluble chelate complexes with the metals and effectively retard redeposition of the poisoning metals on the catalyst surface once they are brought into solution. The chelating agents which are employed in this invention contain oxygen and frequently nitrogen as well. Among the nitrogen-containing agents which are employed the most popular is ethylene diamine tetraacetic acid (EDTA). Also, triethanolamine in alkaline solutions; polyethylene polyamino acids such as triethylene tetraamine tetraacetic acid and its homolog amino acids. Certain epoxyamine acetic acid salts; amino derivatives of N-alkyl substituted aspartic acids and their functional derivatives and tri-ammonium salts of mono-isopropanol ethylene diamine triacetic acid have been reported as able to chelate heavy metal ions.

Other organic chelating agents are those organic acids having an available OH group alpha to a carboxyl group. The OH group may be an alcoholic hydroxyl or may be contributed by a second carboxylic group. Generally the COOH and OH groups while being separated by about 1–4 carbon atoms and will be in cis relationship, that is, capable of forming an inner anhydride, such as in maleic acid. The trans form of this acid, fumaric acid, does not chelate. The chelating agent molecule may be saturated or unsaturated and may be substituted with further COOH and/or OH groups or other substituents which do not have an adverse effect, such as alkyl or alkoxy, but should not contain substituents which may retard water solubility below the small solubility required to achieve the dilute chelating solution required for effectiveness. Among the suitable hydroxy and/or polycarboxylic acids are citric acid, tartaric acid, lactic acid and glycolic acid, while suitable dicarboxylic acids include malic and maleic acids. The chelating solution is neutral or acid, with a pH of about 1–7, advantageously 1–3. For reasons of water-solubility at this pH, as well as for economic reasons, citric acid or other hydroxy carboxylic acids are the preferred chelating agents. The chelating agent solution can by recycled after removal from the catalyst by passage through a suitable ion exchanger.

A number of reducing agents are available for use in the aqueous wash medium. Such agents are at least partially water-soluble, have a single electrode reduction potential at 25° C. of less than about 0.8 volt and do not leave a contaminant on the catalyst. Preferably sulfur-containing inorganic reducing agents are employed, of which H_2S is the most commercially feasible. Generally, a pH below about 4 or even 5 is used in the reducing aqueous medium for best metals removal. H_2S gas may be bubbled into the water to make the reducing medium and this gas is generally readily available in the petroleum refinery. Even the effluent from the sulfider of the demetallization system contains sufficient H_2S for this purpose. Sulfurous acid may be used in the aqueous medium but it is weak and requires considerable reagent and a low pH for good removal. Hydrosulfite is a stronger reducing agent and is effective at a higher pH, but is more expensive. Other reducing agents of a wide variety are effective in metal removal. Hydroxylamine, hydrazine, sodium or ammonium hypophosphite, and hydrogen iodide are effective but more expensive.

The pH of the aqueous reducing medium is below about 5. Above this pH metals removal is not too efficient with most reagents and with some, metal sulfides tend to precipitate above this pH. At a low pH, below about 2.5, the loss of alumina from the catalyst may become significant especially when the pH is below about 2.0, so that the preferred pH of the aqueous medium is about 2.5 to 4. The chlorine entrained in the catalyst is frequently sufficient to impart the proper pH to the aqueous medium, or HCl or NH_4OH may be added to the medium in amounts desired for proper pH adjustment.

When a gaseous reducing agent is supplied to the catalyst between the chlorination and aqueous wash treatments it may be any of the reducing agents mentioned above which is volatile at the reaction conditions. H_2S gas, for example, may be employed at a temperature of about 100 to 500° F., preferably at about 200° F. A very high temperature should be avoided in order to avoid sulfiding the metal contaminants. Hydrogen gas may be used in this temperature range, but its effect on vanadium removal is negligble, although it aids iron removal. The use of a gaseous reducing agent is followed by a water wash.

After any of the aqueous wash treatments the catalyst may be given an ammonium wash as described above. After the ammonium wash, or after the final treatment which may be used in the catalyst demetallization procedure, the catalyst is conducted to a conversion system, although it may be desirable first to dry the catalyst filter cake or filter cake slurry at say 250 to 450° F. and also, prior to reusing the catalyst in the conversion operation it can be calcined, say at temperatures usually in the range of about 700 to 1300° F. Drying the catalyst after washing, at a low temperature, for example, about 400° F., removes residual chloride on the catalyst, but the rate of evolution increases at higher temperatures. A short calcination at 1000° F. or higher effectively lowers chloride to an acceptable level (0.005%) and it is possible that any chloride can be removed simply by adding the treated catalyst to the conversion unit regenerator.

As mentioned, the catalyst to be treated may be removed from the hydrocarbon conversion system—that is, the stream of catalyst which in most conventional procedures is cycled between conversion and regenerating operations—before the poison content reaches about 5000 to 10,000 p.p.m. Preferably less than 2000 p.p.m. each of nickel and/or vanadium is allowed to accumulate. Also, as mentioned, the catalyst is removed for demetallization after it is contaminated with at least about 800 p.p.m. nickel and/or 1000 p.p.m. vanadium, if demetallization is to produce a significant improvement in the cracking.

In practicing this invention at the refinery, a portion of the poisoned catalyst can be removed from the hydrocarbon conversion system after being regenerated and given a high temperature treatment with an oxygen-containing gas at an elevated temperature for the length of time found to be sufficient to increase vanadium removal without damaging the catalyst. Then the catalyst may be maintained in a hydrogen sulfide or a hydrogen sulfide-inert gas mixture for one to three hours at temperatures approximating 1150° F. The sulfiding gas is purged from the catalyst by an inert gas, perhaps at a cooler temperature, then contacted with chlorine in the temperature range outlined and washed with the aqueous medium containing H_2S. The treated catalyst, usually reduced in contaminating metals to below about 1000 p.p.m. each of vanadium and nickel preferably below about 800 p.p.m. nickel is returned to the cracking system, for example, to the regenerator, reducing greatly the new catalyst requirement. The amount of Ni, V, or Fe removed in practicing the procedures outlined or the proportions of each which are removed may be varied by the proper choice of treating conditions. It may prove advantageous, sometimes to repeat the treatment to reduce the metals to an acceptable level, perhaps with variatons where one metal is greatly in excess. The duration of each treatment may vary with the temperature, manipulations, and other factors employed in the treatment, but in general each treatment step is prolonged for a time necessary to give a significant result, that is, to give more metal removal than would be obtained had the step not been performed.

The apparatus used to perform the process of the invention generally is suitable for conducting part or all of the cracking and demetallization procedures with fluidized beds of finely divided catalyst in the various operations. When fluidized manipulations are to be used, the various gas or vapor treating agents described may be supplemented with inert fluidizing gases, such as nitrogen, where the flow of active gas is not sufficient for fluidization.

Examples

The following examples are illustrative of the invention but should not be considered limiting. In the demetallization operations described below washing was conducted with a 20% slurry of catalyst in an aqueous medium comprising tap water. The washing was followed by filtration and reslurrying twice in tap water before a final rinse. Each catalyst sample was dried in an oven at about 500° F. before analysis and test cracking.

A semi-synthetic catalyst prepared by precipitating alumina on acid-treated clay from a solution of $NH_4Al(SO_4)_2$ was used in a commercial catalytic cracking conversion unit, using conventional fluidized catalyst techniques, including cracking and air regeneration to convert a feedstock (A) comprising a blend of Wyoming and Mid-Continent gas oils containing 0.3 p.p.m. NiO, 0.6 p.p.m. V_2O_5 and about 0.7 weight percent sulfur. This gas oil blend had a gravity (API) of 26, and a boiling range of about 500 to 1000° F. When this catalyst had a poisoning metals content of 451 p.p.m. NiO, 686 p.p.m. V_2O_5 and 0.318% Fe, a batch of this base catalyst was removed from the cracking system after regeneration. A portion of this base catalyst was used to test-crack a petroleum hydrocarbon East Texas gas oil fraction (feedstock B) having the following approximate characteristics:

IBP (° F.)	490–510
10%	530–550
50%	580–600
90%	650–670
EP	690–710
Grav. (° API)	33–35
Visc. (SUS) at 100° F.	40–45
Aniline point, ° F.	170–175
Pour point, ° F.	35–40
Sulfur, percent	0.3

The results are given in Table I below. Another portion of this base catalyst was treated with air for one hour at 1275° F., with H_2S for one hour at 1150° F. and with chlorine gas for 10 minutes at 600° F. It was then washed with a citric acid solution, dried, calcined and sent to cracking of feedstock B. The metals removal and cracking results are given in Table I below.

TABLE I

	Untreated	Treated
Metal Analysis:		
P.p.m. NiO	551	147
P.p.m. V_2O_5	686	590
Percent Fe	0.318	0.229
Percent Metal Removed:		
Ni	----------	67
V	----------	14
Fe	----------	28
Cracking Results:		
Relative Activity	24.2	26.5
Distillate plus Loss	26.5	28.1
Gas Factor	1.21	1.26
Coke Factor	1.03	0.91
Gas Gravity	1.24	1.26

These results show that at a moderate level of metal on this catalyst the cracking results are not greatly affected by variations in the metal content and that demetallization, therefore, while it does serve to remove metals has a relatively insignificant effect on the cracking results. Another batch of catalyst was poisoned by use in cracking a residual hydrocarbon feedstock containing about 20 p.p.m. Ni and 30 p.p.m. V to the metal level shown in Table II. A batch of this poisoned catalyst was sent to test cracking of feedstock B while the remaining amount was held in air for one hour at 1275° F., sulfided for one hour with H_2S at 1150° F. and treated with chlorine gas for 10 minutes at 600° F. This treated portion is divided into two samples, of which sample D is treated with a citric acid solution and sample E is treated with a hydrogen sulfide solution. Each sample, after treatment, was used to test-crack feedstock B. The results are given in Table II below.

TABLE II

Sample	Base	D	E
Metal Analysis:			
P.p.m. NiO	969	339	399
P.p.m. V_2O_5	1,521	938	982
Percent Fe	0.371	0.218	0.209
Percent Metal Removal:			
Ni	-------	65	59
V	-------	37	35
Fe	-------	41	44
Test Cracking:			
RA	24.4	31.7	32.5
D+L	26.6	31.5	32.0
GF	1.73	1.13	1.21
CF	1.30	0.85	0.94
GG	0.93	1.25	1.21

These results show the value of demetallization of this catalyst when the metal level is high and the good cracking results which may be obtained using the process of this invention.

It is claimed:

1. A method for producing gasoline in a hydrocarbon cracking system consisting essentially of a catalytic cracking zone and a catalyst regeneration zone between which catalyst is cycled, which consists essentially of providing said cracking zone with a calcined catalyst consisting essentially of about 10 to 65% alumina, the balance substantially silica, made by coating 100 parts of a solid silica-alumina substrate with about 3 to 100 parts, on a dry basis, of a synthetic hydrous alumina, contacting said catalyst in said cracking zone with a hydrocarbon feedstock heavier than gasoline and containing more than about 5 p.p.m. nickel, which nickel deposits on the catalyst, collecting cracked hydrocarbon products including gasoline, contacting catalyst in said

regeneration zone with a combustion supporting gas whereby carbon is oxidized and thereby removed from the catalyst, bleeding from the cracking system a portion of catalyst containing at least about 800 p.p.m. nickel, sulfiding bled catalyst by contact with a sulfiding vapor at about 700–1300° F., chlorinating sulfided catalyst by contact with chlorine vapor at about room temperature to 900° F., said sulfiding and chlorinating serving to enhance subsequent nickel removal, washing the catalyst with an aqueous medium selected from the group consisting of (1) a solution having a pH below about 5 and containing a reducing agent having a single electrode potential less than about 0.8 volt, (2) a solution containing a chelating agent for the contaminant, and (3) when the catalyst has been contacted between chlorination and washing with a vaporous reducing agent having the properties described, water, and returning resulting denickelized catalyst to a hydrocarbon cracking system.

2. The method of claim **1** in which the catalyst is washed with an aqueous solution containing a chelating agent for the contaminant.

3. The method of claim **2** in which the chelating agent is an organic material containing oxygen and nitrogen.

4. The method of claim **2** in which the chelating agent is an organic acid having an available OH group alpha to a carboxyl group.

5. The method of claim **1** in which the catalyst is washed with an aqueous solution having a pH below about 5 and containing a reducing agent having a single electrode potential less than about 0.8 volt.

6. The method of claim **5** in which the reducing agent is H_2S.

7. The method of claim **1** in which the chlorinated catalyst is contacted with a vaporous reducing agent having a single electrode potential of less than about 0.8 volt and is washed with water.

8. The method of claim **7** in which the reducing agent is H_2S.

9. A method for producing gasoline in a hydrocarbon cracking system consisting essentially of a catalytic cracking zone and a catalyst regeneration zone between which catalyst is cycled, which consists essentially of providing said cracking zone with a calcined catalyst consisting essentially of about 15 to 50% alumina, the balance substantially silica, made by coating about 100 parts of a solid silica-alumina substrate with about 10 to 20 parts, on a dry basis, of a synthetic hydrous alumina, contacting said catalyst in said cracking zone with a hydrocarbon feedstock heavier than gasoline and containing more than about 5 p.p.m. nickel, which nickel deposits on the catalyst, collecting cracked hydrocarbon products including gasoline, contacting catalyst in said regeneration zone with a combustion supporting gas whereby carbon is oxidized and thereby removed from the catalyst, bleeding from the cracking system a portion of catalyst containing about 800 to 2000 p.p.m. nickel, sulfiding bled catalyst by contact with a sulfiding vapor at about 700–1300° F., chlorinating sulfided catalyst by contacting with chlorine vapor at about room temperature to 900° F. said sulfiding and chlorinating serving to enhance subsequent nickel removal, washing the catalyst with an aqueous medium selected from the group consisting of (1) a solution having a pH below about 5 and containing H_2S as a reducing agent, (2) a solution containing an organic chelating agent for the nickel and (3) when the chlorinated catalyst has been contacted with H_2S vapor as a reducing agent before washing, water, to remove nickel and returning resulting denickelized catalyst to a hydrocarbon cracking system.

10. A method for producing gasoline in a hydrocarbon cracking system consisting essentially of a catalytic cracking zone and a catalyst regeneration zone between which catalyst is cycled, which consists essentially of cracking at elevated temperature in said cracking zone, a hydrocarbon feedstock heavier than gasoline and containing more than about 5 p.p.m. nickel and more than about 5 p.p.m. vanadium with a calcined catalyst consisting essentially of about 10 to 65% alumina, the balance substantially silica, made by coating 100 parts of a solid silica-alumina substrate with about 3 to 100 parts, on a dry basis, of a synthetic hydrous alumina, collecting the products of such cracking, removing catalyst from the cracking system after it accumulates at least about 800 p.p.m. nickel, contacting the bled substantially carbon-free catalyst for at least about 15 minutes with a gas containing molecular oxygen at a temperature of at least about 1150° F. to increase subsequent vanadium removal from the catalyst, sulfiding bled catalyst by contact with sulfiding vapor at about 700–1300° F., chlorinating sulfided catalyst by contact with chlorine vapor at about room temperature to 900° F., said sulfiding and chlorinating serving to enhance subsequent nickel removal and washing the catalyst with an aqueous medium selected from the group consisting of (1) a solution having a pH below about 5 and containing a reducing agent having a single electrode potential less than about 0.8 volt, (2) a solution containing a chelating agent for the contaminant, and (3) when the catalyst has been contacted between chlorination and washing with a vaporous reducing agent having the properties described, water, and returning catalyst of reduced metals content to the cracking system.

References Cited by the Examiner

UNITED STATES PATENTS

2,371,069	3/1945	Ruthruff	252—455
2,466,050	4/1949	Shabaker et al.	208—120
2,488,718	11/1949	Forrester	208—113
3,010,914	11/1961	Braithwaite et al.	208—120
3,060,117	10/1962	Payne	208—305
3,122,497	2/1964	Erickson	208—120
3,158,565	11/1964	Sanford et al.	260—888

DELBERT E. GANTZ, *Primary Examiner.*

ALPHONSO D. SULLIVAN, DANIEL E. WYMAN, *Examiners.*

A. RIMENS, *Assistant Examiner.*