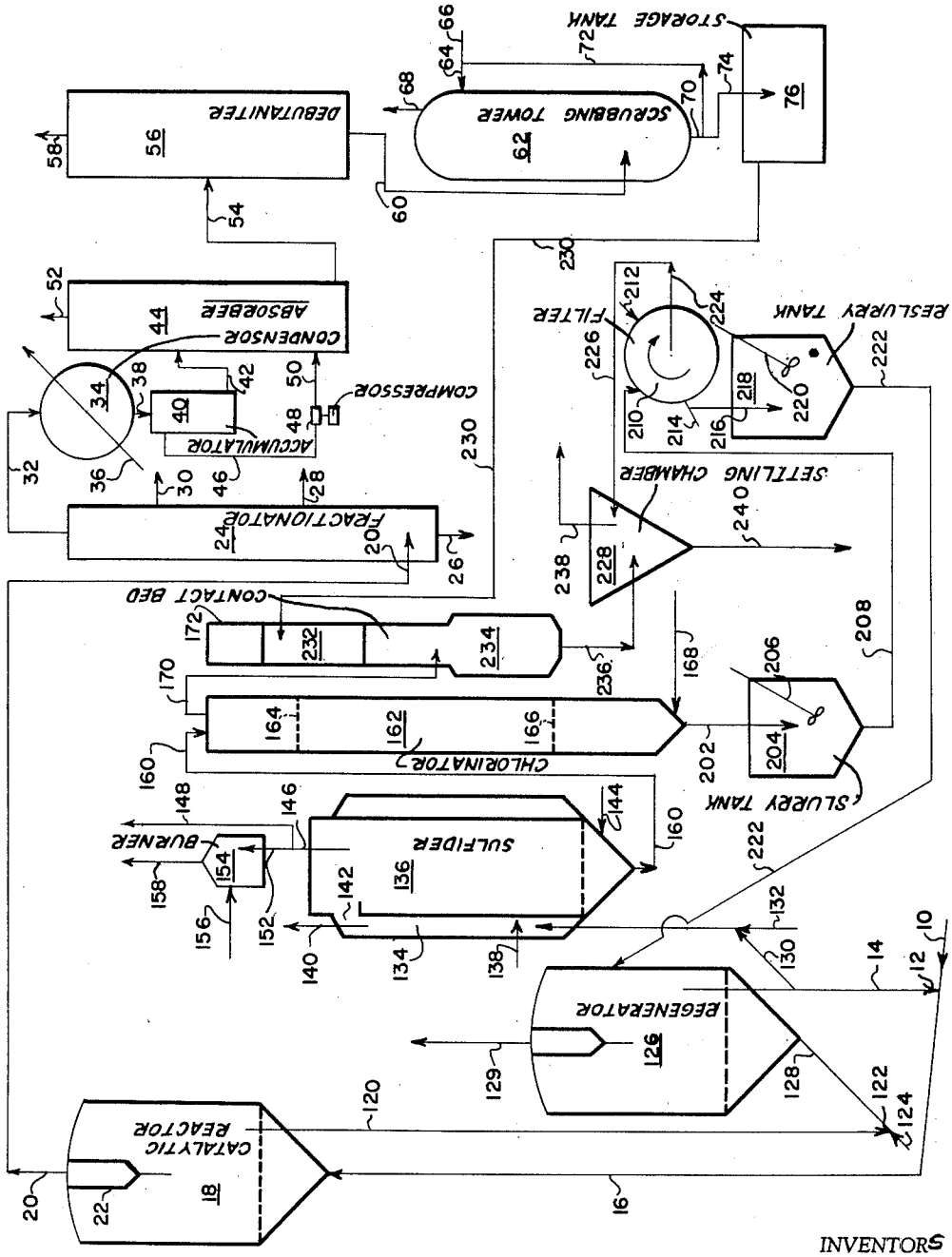
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CATALYST DEMETALLIZATION EFFLUENT TREATING

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CATALYST DEMETALLIZATION EFFLUENT TREATING

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This invention is a method for producing and treating gasoline which employs catalytic cracking of a feedstock containing metal contaminants, demetallization of the catalyst and destruction of poisonous materials and neutralization of waste materials from the demetallization by waste materials from the gasoline treatment.

Catalytically promoted methods for the chemical conversion of hydrocarbons include cracking of heavier hydrocarbon feedstocks to produce hydrocarbons of preferred octane rating boiling in the gasoline range. Feedstocks to these processes comprise normally liquid and solid hydrocarbons which are fed, usually in the fluid, i.e. liquid or vapor, state to one of a variety of solid oxide catalysts generally at temperatures of about 750 to 1100° F., preferably about 850 to 950° F., at pressures up to about 2000 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.

Petroleum refiners try to avoid the use of cracking feedstocks which are known to contain significant amounts of metals since most of these metals, when present in a stock, either naturally or through contact with metallic apparatus, deposit as a non-volatile compound on the catalyst during the conversion processes so that regeneration of the catalyst to remove coke does not remove these contaminants. It is to be understood that the term "metal" used herein refers to both elemental metals and metal compounds. In particular, iron, nickel, vanadium and copper from a feedstock deposit on the catalyst markedly altering the selectivity and activity of cracking reactions, generally producing a higher yield of coke and hydrogen at the expense of desired products, such as gasoline, butylenes 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 volume percent when the amount of nickel on the catalyst increased from 55 p.p.m. to 645 p.p.m. and the amount of vanadium from 145 p.p.m. to 1480 p.p.m. in fluid catalytic cracking of a feedstock containing some metal contaminated marginal stocks.

Rather than permit metals levels on the catalyst to increase when a poisonous feed must be used, many refiners merely replace contaminated catalyst frequently with virgin unpoisoned catalyst. However, it has been found possible to employ specialized techniques to remove metal contaminants from a poisoned cracking catalyst. It has been found, for example, that a catalyst which has been contaminated with Fe, Ni and/or V by use in the high temperature conversion of feedstocks containing these metals may be demetallized by chlorination treatment followed by an acidic aqueous wash. This invention uses such demetallization techniques and also disposes of the waste acid gases and liquids from the demetallization by exploiting the acid values.

Solid oxide catalyst 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-alumina, silica-magnesia or silica-zirconia, etc., compositions in a state of very slight hydration and containing small amounts of acidic oxide promoters in many instances. The oxide catalyst may be alumina- or 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. 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 hydrate materials of foreign constituents such as alkaline 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. Popular synthetic gel cracking catalysts generally contain about 10 to 30% alumina on silica. Two such catalysts are "Aerocat" which contains about 13% Al_2O_3, and "High Alumina Nalcat" which contains about 25% Al_2O_3, with substantially the balance being silica. The catalyst may be only partially of synthetic material; for example, it may be made by the precipitation of silica-alumina on an activated clay, such as kaolinite or halloysite. One such semi-synthetic catalyst contains about equal amounts of silica-alumina gel and clay. Such commercially used cracking catalysts are the result of years of study and research into the nature of cracking catalysis, and the cost of these catalysts is not negligible. The expense of such catalysts, however, is justified because the composition, structure, porosity and other characteristics of such catalysts are rigidly controlled so that they may give optimum results in cracking. It is important therefore, that removing poisoning metals from the catalyst does not jeopardize the desired chemical and physical constitution of the catalyst. Although methods have been suggested in the past for removing poisoning metals from a catalyst which has been used for high-temperature hydrocarbon conversions, for example, the processes of U.S. Patents 2,488,718; 2,488,744; 2,668,798 and 2,693,455; the processes used herein are effective to remove metals without endangering the expensive catalyst.

In this invention, the hydrocarbon petroleum oils utilized as feedstock for a conversion process may be of any desired type normally utilized in catalytic conversion operations, and will generally contain metal contaminants, sometimes as much as 3%. The feedstock generally boils primarily in the gas-oil range or higher, that is, from about 400 to 1400° F. The catalyst may be used as a fixed, moving or fluidized bed or may be in a more dispersed state. In fluid processes gases are used to convey the catalyst and to keep it, during reactions, 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 200 microns. Other processes use catalysts in the form of beads of about ⅛ to ½ inch in diameter, or in the form of tablets or extruded pellets.

The catalytic cracking system includes the cracking zone and a regeneration zone wherein carbon deposited on the catalyst is burned off by exposing the catalyst to air at a temperature of about 900 to 1400° F. In the process of this invention, gas oil containing metal poisons and, if desired, heated to the vapor state, e.g. to a temperature of about 400 to 800° F., is fed to a reactor in combination with regenerated catalyst. The cracked products pass overhead to a fractionator which separates gasoline and lower boiling materials from cycle oil and

bottom products which can be blended into fuel oils, further processed, or recycled to the cracking reactor. The fractionator overhead includes gas and gasoline which are passed through a condenser to several separatory stages for separating out fixed gases from the gasoline fraction. The gasoline fraction, for removal of oxygenated and sulfurous compounds such as phenols and hydrogen sulfide which are considered deleterious, is scrubbed with a circulating stream of NaOH solution, generally at about 15–25° Baumé to convert these materials to sodium compounds which are readily separable from the gasoline with the aqueous caustic phase. The gasoline from caustic treating can be further refined or sent directly to blending with other components of the finished gasoline.

The aqueous caustic may be recycled through the gasoline scrubbing zone until it substantially loses its activity for removing gum formers. The resulting aqueous solution or suspension of phenolics and other organo-sodium materials is usually forbidden by law to be dumped into streams, etc., and a treatment of these wastes is desirable to insolubilize the organic materials and thereby provide for separation of the bulk of the waste as a more or less innocuous aqueous solution of inorganic materials. Also, the organic materials may be saleable for certain end uses.

Various techniques have been suggested to remove the metal contaminants from synthetic gel cracking catalysts. For example, the processes of copending applications, Serial Nos. 763,834, filed September 29, 1958 now abandoned; 849,199, filed October 28, 1959; 842,618, filed September 28, 1959 now abandoned; and 19,313, filed April 1, 1960 now abandoned, are illustrative of such processes and are incorporated herein by reference. A poisoned catalyst may be reduced in nickel content by an aqueous wash when nickel contaminants are put into a water-dispersible form by treating a sulfided nickel-contaminated catalyst. Sulfiding may be performed as disclosed in copending application Serial No. 763,834, filed September 29, 1958; or Serial No. 842,618, filed September 28, 1959. It has been found that iron and vanadium may be removed from a catalyst by converting the metals into volatile compounds; a chlorination treatment can convert iron and vanadium to volatile chlorides as reported in copending application Serial No. 849,199, filed October 28, 1959. Also as pointed out in copending application Serial No. 19,313, filed April 1, 1960, a preliminary treatment of the catalyst with molecular oxygen-containing gas is of value in increasing the quantity of vanadium removed.

This invention advantageously includes demetallization effected by chlorination of the metal contaminated catalyst. Chlorination may be combined with other procedures for improved demetallization of catalysts which have become poisoned in the cracking process of the invention. For example, the chlorination may be preceded by sulfiding the poisoning metals to improve the removal of nickel poisons in subsequent steps; the treatment with the chlorinating agent may be followed by treatment with an inert vapor to enhance volatilization of the iron and vanadium chlorides formed. These iron and vanadium chlorides are essentially acidic in character and cannot be released to the atmosphere because they readily condense in the vicinity of the apparatus when the effluent vapor cools. Also, the chlorinator effluent may contain poisonous gases such as phosgene.

A conversion to vanadium chloride after the high temperature oxygen treatment preferably makes use of vapor phase chlorination at a moderately elevated temperature, up to about 700° or even 1000° F., wherein the catalyst composition and structure is not materially harmed by the treatment and a substantial amount of the poisoning metals content is converted to chlorides. The conversion to chloride may be performed after sulfiding the poisoning metals, as described below. The chlorination takes place at a temperature of at least about 300° 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 or sometimes HCl, preferably in combination with carbon or sulfur. Such reagents include molecular chlorine but preferably are mixtures 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.

The stoichiometric amount of chlorine required to convert iron, nickel and vanadium to their most highly chlorinated compounds is the minimum amount of chlorine ordinarily used and may be derived from free chlorine, combined chlorine or the mixture of chlorine with a chlorine compound promoter described above. However, since the stoichiometric amount of chlorine frequently is in a neighborhood of only 0.001 g./g. of catalyst, a much larger amount of chlorine, say about 1–40 percent active chlorinating agent based on the weight of the catalyst is generally used. The amount of chlorinating agent required is increased if any significant amount of water is present on the catalyst so that substantially anhydrous conditions preferably are maintained as regards the catalyst as well as the chlorinating agent. The 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 amount of promoter may vary depending upon the manipulative aspects of the chlorination step, for example, a batch treatment may sometimes require more promoter than in a continuous treatment for the same degree of effectiveness and results. 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 make 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 vapors. Excesses of the chlorinating vapors as well as other acid-acting materials will be present in the chlorinator effluent. These vapors generally are forbidden to be released to the atmosphere or released to sewage systems as liquids without further treatment to mitigate their polluting effects. Treatment with the chlorinating vapor may not remove from the catalyst all of the iron and vanadium chlorides formed. The chlorination may therefore be followed or interrupted by a purge of the catalyst with inert gas such as nitrogen or flue gas at a temperature sufficiently high to vaporize the chlorides.

After chlorination nickel may be removed from the catalyst by a liquid aqueous wash. This aqueous medium, for best removal of nickel is generally somewhat acidic, and this condition may be brought about, at least initial-

ly, by the presence of an acid-acting salt or other material entrained 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. 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. However, contact periods as low as 1 minute have been satisfactory as well as washing for a period of about 2–5 hours or longer. The wash solution also provides another waste disposal problem. The acidity of the waste wash solution as well as of the waste chlorinator effluent gas stems primarily from chlorine, ionizable chlorine compounds and materials which decompose to either of these, other materials in these mixtures being in general too weakly acidic to be significant waste disposal problems. Also, since practically all of the chlorine and chlorine compounds fed to the chlorinator reappear in either the waste gas or waste liquid, the acidity of the wastes is determined by the chlorine fed to the chlorinator. Thus the agent used to neutralize these acid wastes should provide two moles of a univalent base for each mole of molecular chlorine, or equivalent amounts for ionizable chlorides supplied to the chlorinator.

As mentioned above, the poisoned catalyst may be sulfided before chlorination. 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 0.5–25 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 suifiding 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 described demetallization procedures produce significantly greater removal of vanadium when, upon removal of the poisoned catalyst from the conversion system, it is regenerated, given a treatment at elevated temperatures with molecular oxygen-containing gas, and washed with the liquid aqueous solution before returning the catalyst to the hydrocarbon conversion system. Ordinarily, the catalysts are treated before the poisoning metals have reached an undesirably high level, for instance, about 2%, generally no more than about 1% maximum, content of vanadium. Prior to oxygen treatment, subjecting the poisoned catalyst sample to magnetic flux may be founde 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 1200° F., more usually about 1000 to 1150° 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 on the order of about six minutes and the oxygen content of the effluent gases from the regenerator is desirably less than about ½%. When later oxygen treatment is employed, the regeneration of any particular quantum of catalyst is generally regulated to give a carbon content of less than about 0.5%.

Treatment of the regenerated catalyst with molecular oxygen-containing gas is described in copending application Serial No. 19,313, filed April 1, 1960. The temperature of this treatment is generally 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. 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. In any event, after carbon removal, the oxygen treatment of the essentially carbon-free catalyst is at least long enough to convert a substantial amount of vanadium to a higher valence state, 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 treatment of the vanadium-poisoned catalyst with molecular oxygen-containing gas prior to sulfidation and/or chlorination is preferably performed at a temperature of about 1150 to 1350 or even as high as 1600° F. and at least about 50° F. higher than the regeneration temperature. Little or no effect on vanadium removal is accomplished by treatment at temperatures significantly below about 1000° F., even for an extended time. The upper temperature, to avoid undue catalyst damage, will usually not materially exceed about 1600 or 1800° 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. The length of the oxygen treatment 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 a relatively static apparatus such as a muffle furnace, the effectiveness of the treatment can increase with the time over a rather extended period; in other types of apparatus, however, such as a flow reactor, where there is more thorough contact of catalyst and gas, little increase in effectiveness was observed after about four hours of treatment.

The oxygen-containing gas used in the treatment contains molecular oxygen as the essential active ingredient. The gas may be oxygen, or a mixture of oxygen with inert gas, such as air or oxygen-enriched air and there is little significant consumption of oxygen in the process. 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. As the oxygen partial pressure increases the time needed to increase the valence of a given amount of vanadium in general decreases. The factors of time, partial pressure and extent of vanadium conversion may be chosen with a view to the most economically feasible set of conditions. It is preferred to continue the oxygen treatment for at least about 15 or 30 minutes with a gas containing at least about 1%, preferably at least about 10% oxygen.

In this invention the waste caustic from gasoline finishing is used to destroy poisonous materials such as phosgene and to neutralize the gaseous and aqueous acid-acting

wastes from demetallization. The spent caustic may have a pH of about 7 to 12 when it is exhausted; catalyst slurry wash water may have a pH of about 2 to 7 and the rinse water may have a pH of about 4 to 7. The effectiveness of the caustic however, is greater than pH test methods indicate; the generally organic or other slightly ionized anions with which sodium is combined in the spent caustic will tend to precipitate from the solution when converted to the acid, freeing further sodium ions for reaction with waste inorganic strong acid-acting materials. Thus, the waste caustic solution has an effectiveness for neutralizing strong acid equivalent to its original strength before use in gasoline finishing. The amount of caustic waste mixed with acid waste will vary depending on the conditions of the processing scheme. However, in general, as mentioned above, enough waste caustic will be used to supply two moles of sodium for each mole of chlorine gas employed in the demetallization. The extent of caustic addition will be sufficient to bring the aqueous wastes to a substantially neutral condition and the acid waste will in general be sufficient to spring substantially all of the organic materials from the waste caustic. The aqueous caustic decomposes phosgene to HCl and CO_2. In the practice of this invention it may sometimes be found that the caustic wastes are insufficient for complete neutralization of the acids. In such a situation, additional caustic or other alkaline material may be added to the neutralization mixture. Alternatively, the rate of caustic replacement in the gasoline finishing can be increased.

The process of the invention will be better understood by reference to the accompanying schematic drawing which illustrates the process in an embodiment which uses fluidized beds of catalyst. Catalyst conveying in such procesing schemes is generally performed by gravity and by air which is usually supplied by blowers, not shown in the drawing.

Gas oil containing metal poisons is vaporized and conducted into the system by conduit 10, from an external source, not shown. At the juncture 12 with the regenerator standpipe 14, gas oil vapors pick up regenerated catalyst and convey it through the conduit 16 to the fluid cracking reactor 18 where a significant amount of the gas oil is converted to light hydrocarbon gases and materials boiling in the gasoline range. These essentially hydrocarbon products, with a small amount of oxygen, sulfur, etc., containing materials leave the cracker through the effluent conduit 20 after perhaps passing through a cyclone separator 22 which disentrains catalyst fines from the product vapors.

The product is brought by conduit 20 to the fractionator 24 which separates the product mixture on the basis of the boiling points of the constituents. The bottoms (nonvaporized) fraction is removed from the fractionator by the line 26, heavy cycle oil by the line 28 and light cycle oil by the line 30. Each of these fractions is capable of certain immediate end uses, but they can be recycled singly or combined to the craking zone 18.

The gasoline fraction, containing lower boiling materials, is conducted by line 32 to condenser 34 where, perhaps by indirect heat exchange with water from a conduit 36, the greater part of the normally liquid fraction is condensed. The condenser effluent may then pass by means of line 38 to an accumulator 40 where the effluent is held in a quiescent state to allow fixed gases to disentrain themselves from the liquid fractions which are removed by line 42 to the absorber 44. In the absorber, gas from line 46 of accumulator 40, condensed by compressor 48 and conducted by line 50, passes countercurrent to the liquid fraction to extract further dissolved gases from the liquid fraction. Substantially all the methane and ethane are thus removed from the liquid fraction by the line 52. The line 54 conveys the liquid fraction to the debutanizer 56 where the C_4 materials are removed and carried away by line 58.

Gasoline is conveyed from debutanizer 56 by the line 60 to the scrubbing tower 62. An aqueous caustic solution is fed to the top of the scrubber by line 64, perhaps from the external source 66, where it passes countercurrently to the gasoline, removing oxygenated and/or sulfur-containing materials. Finished gasoline passes out of the scrubber by line 68 to use. The caustic is drawn from the bottom of the scrubber by line 70 whence it may be recycled through line 72 to line 64, or, if exhausted, drawn off by line 74 to storage in the tank 76.

Catalyst from cracking reactor 18, contaminated with coke and metal poisons, is drawn off, more or less continuously, through the standpipe 120. At the juncture 122 the catalyst is met by air from a source 124 which conveys the catalyst to regenerator 126 by means of pipe 128. The air-catalyst mixture arrives, close to the combustion temperature of carbon, in the regenerator where such combustion takes place. This combustion restores or maintains the activity of the catalyst by removing carbon. It will be understood that in this specification and claims "regeneration" refers to this carbon burn-off procedure. In the process of this invention the regeneration conditions, including the rate of withdrawal of catalyst from the cracker and residence time in the regenerator, are generally controlled so that the carbon content of the catalyst leaving the regenerator is less than about 5.0%, preferably less than about 0.5%. Waste gases from the regenerator leave by means of line 129. The catalyst, reduced in carbon content, returns by means of the standpipe 14 to the cracker, as explained above.

The standpipe may be provided with the bleed conduit 130 for withdrawing catalyst to be demetallized. The catalyst may be conveyed to demetallization by air from the line 132. Ordinarily the fraction of regenerated catalyst withdrawn in this slip-stream to demetallization will be regulated to keep catalyst metals poisons from reaching an undersirably high level, for instance, about 2% generally no more than about 0.5% maximum, content of one or both nickel and vanadium calculated as their common oxides. Treatment is usually not warranted unless the catalyst has at least about 25–50 p.p.m. of nickel oxide and/or about 250–500 p.p.m. vanadium pentoxide.

The demtallization comprises one or more procedures which may produce acid-acting waste materials. The amount of Ni, V or Fe removed in practicing any particular procedure or the proportions of each which are removed may be varied by proper choice of procedures and treating conditions. When the catalyst is severely poisoned in relation to the tolerance of the reactor for poison, it may be necessary to repeat some or all of the treatment when batch operation are employed, or to increase the demetallization rate, that is, the proportion of catalyst sent to demetallization, in a continuous process, to reduce the metals to an acceptable level, perhaps with variations where one metal is greatly in excess. The demetallization procedure illustrated makes provision for heating, sulfiding, chlorinating, washing and filtering the catalyst before its return to the cracking system in a water slurry, but it is to be understood that this series of steps is illustrative and that this invention may include other demetallization procedures as well as procedures wherein some of the illustrated steps are omitted.

In the embodiment of this invention shown in the drawing, the catalyst passes through conduit 130 to an outer chamber 134 of the sulfider 136. The catalyst particles and the sulfider itself are raised to the sulfiding temperature of say about 1150° F., advantageously by burning a fuel in the bed of particles in this chamber. The fuel, with or without the addition of combustion supporting gas, may be supplied by the line 138 and the exhaust gas may be vented by the line 140. The heated catalyst particles may flow into the sulfiding chamber as through the opening 142. A sulfiding gas, e.g., H_2S or CS_2 is passed to the bottom of the sulfider 136 by the line 144. Exhaust sulfiding gas is passed out of the sulfider 136 through the line 146. These gases may be passed di-

rectly through the line 148 to disposal or other use. Alternatively, sulfider effluent may be conducted by line 146 to line 152 to a burner 154. This burner may be supplied with combustion supporting gas by line 156 and with a vent 158 leading to disposal or other use.

Sulfided catalyst is removed from the sulfider 136, preferably at the bottom, by line 160 to the chlorinator 162. The chlorinator is generally an elongated chamber made of Monel or other chlorine resistant material and may be provided with one or more internal grids 164, 166 for gas distribution and break-up of catalyst particle agglomerates. The chlorinating agent is brought to the chlorinator 162 from the conduit 168. The agent may be preheated if desired and generally will comprise a mixture of elemental chlorine with a promoter as described above. Excess chlorinating vapor is withdrawn from the chlorinator by the line 170 for conduction to the contact tower 172.

The chlorinated catalyst leaves the chlorinator 162 by the line 202 to the slurry tank 204 which is advantageously provided with stirrer 206. In the slurry tank the chlorinated catalyst is admixed with a large volume of water which may contain acidifying agents with or without ammonium ions, as described above. This very dilute slurry may be removed from the tank 204 and brought through the line 208 to the filter 210 which may advantageously be a rotary vacuum drum filter as shown, or a pan filter. The cake of catalyst particles on the filter may be rinsed by water from line 212, scraped from the filter by doctor blade 214 and fall through the path or conduit 216 into the reslurry tank 218 which advantageously is provided with a stirrer 220, from which the catalyst may be returned, for example, to the regenerator by the line 222 as a water slurry. Alternatively, the route of catalyst back to the regenerator may be by means of drying and calcination zones to remove free and combined water from the catalyst. Wash water and rinse water removed from the catalyst slurry are conveyed from the filter by line 224 to the line 226 for introduction into the neutralizing and separating chamber 228.

Spent caustic is conveyed from storage tank 76 by line 230 to the upper portion of contact tower 172 which may be provided with solid inert contact material for instance in a bed 232. In this tower, the aqueous waste caustic solution contacts the acid-acting gaseous chlorination effluent from line 170. The aqueous solution decomposes some components, e.g., phosgene, neutralizes the acid components of these gases and scrubs out such materials. The neutralization also tends to precipitate organics from the aqueous phase. Inert gases pass from tower 172 through line 174. The liquid stream passes from the bottom 234 of tower 172 throngh the line 236 and to the chamber 228 accompanied by aqueous wash and rinse fluids from filter 210. In the neutralizing and settling chamber 228, the mixed fluids settle into an upper organic layer comprising phenolics, etc., which may be drawn off by line 238 for recovery, if desired, or burning, and a lower aqueous layer comprising mostly water and inorganic salts which may be sent to sewage, usually without further treatment, by line 240. In some instances the organic layer settles to the bottom of chamber 228 so that the organic material is drawn off at line 240 and the aqueous solution through line 238.

Example

A gas oil containing about 0.16 p.p.m. Ni, 1.3 p.p.m. Fe and 0.93 p.p.m. V had an API gravity of about 23.4°, a Ramsbottom carbon of about 0.477 weight percent, a viscosity of about 44.3 seconds Saybolt Universal at 210° F., and an initial boiling point above about 420° F. at atmospheric pressure, was preheated to about 660° F., and introduced into a fluid catalytic cracker mixed with a finely divided cracking catalyst at a presure of about 10 p.s.i.g. The catalyst introduced into the feed line was a 26.4% Al_2O_3, silica-alumina "Nalcat" contact cracking catalyst having fluidizable particle size as hereinbefore described. The feed attained a temperature of about 911° F. in the reactor and had a space velocity of about 5.2 pounds of oil per hour per pound of catalyst.

The cracked products were introduced into a fractionator where the products were separated into a cycle oil fraction boiling above about 400° F., a gas fraction (C_3 minus) and a C_4 to 430° F. end point gasoline which comprised 61 weight percent of the cracker effluent. The gasoline contains about 0.16% oxygenated or sulfur-containing materials which are removed by scrubbing with a caustic soda solution of about 20° Bé. Spent caustic is passed to a contact tower.

A stream of catalyst was continually removed from the reactor and sent to a regenerator where it was contacted with air at about 1050° F. to burn off the carbon. The regenerated catalyst was then returned to the cracking reactor. The rate of circulation of catalyst between reactor and regenerator and back to the reactor is about eight times the weight of gas oil charged per hour to the reactor.

A minor portion, totaling about 15% each day, of fluid unit catalyst is continuously removed as a side stream from the regenerator of the cracker where its carbon content is reduced from about 1.1 weight percent to about 0.2 weight percent and is sent to a demetallization system. This catalyst side stream contains about 41 p.p.m. Ni, 505 p.p.m. V and 1200 p.p.m. Fe.

The poisoned catalyst is further regenerated in the catalyst heating portion of the demetallizer, and carbon content reduced to 0.04 weight percent based on the catalyst. It is then fluidized with H_2S gas at a temperature of about 1175° F. for an average reaction time of one hour. The catalyst is then purged with flue gas at a temperature of about 575° F. and chlorinated in a chlorination zone with an equimolar mixture of Cl_2 and CCl_4 at about 600° F. The chlorinator effluent gas has approximately the following composition.

Component:	Weight Percent
Nitrogen	1.7
Carbon dioxide	6.1
Chlorine	4.8
Carbon tetrachloride	24.8
Hydrogen chloride	45.1
Phosgene	13.3
Sulfur dichloride	3.2
Vanadyl trichloride	0.5
Ferric chloride	0.5
	100.0

This chlorinator effluent is passed to the contact tower where it is sent countercurrent to sufficient waste caustic from gasoline finishing to provide about two moles of sodium for each mole of chlorine gas used in the chlorination. The tower effluent comprises a gas consisting mostly of hydrogen sulfide and some nitrogen and carbon dioxide. The contact tower bottoms are sent to a neutralization and settling tank.

After about 1 hour average hold-up time in the chlorinator, the catalyst is removed and slurried with water using 2.3 gallons of water per pound of catalyst. A pH of about 2.2 is imparted to this slurry by chlorine entrained in the catalyst, and the slurry serves to remove nickel chloride. The catalyst, substantially reduced in iron, nickel and vanadium content, is filtered from the wash slurry, dried at about 350° F. and returned to the regenerator. The metals content of the catalyst is reduced by the procedure of this invention from 505 to 395 parts per million vanadium, from 41 to 17 parts per million nickel and from 1200 to 1070 parts per million iron.

The aqueous acidic medium filtered from the slurry is sent to the neutralization and settling tank where it serves to further precipitate organics from the waste

caustic. An organic layer containing phenolics, etc., from the caustic and carbon tetrachloride from the chlorinator effluent gases is removed from the bottom of this settling chamber. An aqueous phase, containing dissolved salts and solid precipitates including Fe, Ni and V hydroxides is removed from the top of the chamber to waste.

It is claimed:

1. In a method wherein a hydrocarbon cracking catalyst is contaminated during the catalytic cracking of a hydrocarbon feedstock, heavier than gasoline and containing nickel and vanadium, in a cracking zone at an elevated temperature to produce gasoline, and nickel and vanadium are deposited on the catalyst, and the gasoline fraction produced by the cracking is treated with caustic, the catalyst is cycled between the cracking zone and a regeneration zone to remove carbon by oxidation, and a portion of the catalyst is bled from the cracking system and subjected to a treatment including contact with a chlorinating vapor to aid in vanadium removal from the catalyst which contact produces an acid-acting effluent; the improvement which comprises combining the acid-acting effluent from the catalyst treatment with an amount of wast caustic from gasoline treating sufficient to neutralize the acid-acting effluent.

2. The method of claim 1 in which the catalyst treatment produces both an acid-acting vanadium containing vapor and an acid acting nickel-containing liquid, both of which are combined with the said caustic.

3. The method of claim 1 in which the demetallization includes contact of the catalyst with an aqueous acidic medium.

4. The method of claim 1 in which said caustic is sodium hydroxide.

5. The method of claim 2 in which said caustic is sodium hydroxide.

6. The method of claim 2 in which the chlorination is effected by contact with an anhydrous chlorinating mixture comprising a chlorinating agent selected from a group consisting of HCl and Cl_2 and a promoter selected from the group consisting of chlorine containing compounds of carbon and sulfur.

7. The method of claim 2 in which the demetallization procedure includes sulfidation.

8. In a method wherein a hydrocarbon cracking catalyst is contaminated during the catalytic cracking of a hydrocarbon feedstock, heavier than gasoline and containing nickel and vanadium poisons, in a cracking zone at an elevated temperature to produce gasoline, and nickel and vanadium are deposited on the catalyst, and the gasoline fraction produced by the cracking is treated with caustic, the catalyst is cycled between the cracking zone and a regeneration zone to remove carbon by oxidation and a portion of the catalyst is bled from the cracking system and subjected to a treatment including contact with a chlorinating vapor to aid in vanadium removal and an aqueous wash which contact produces aqueous acid-acting wastes; the improvement which comprises combining the aqueous, acid-acting wastes from the catalyst treatment with an amount of waste caustic from gasoline treating, having a pH of about 7 to 12, sufficient to neutralize the acid-acting wastes.

9. The method of claim 8 in which the catalyst treatment procedure includes sulfidation.

10. The method of claim 8 in which the catalyst treatment procedure includes contact of the catalyst with an aqueous acidic medium.

11. The method of claim 8 in which the said caustic is sodium hydroxide.

12. In a method wherein a hydrocarbon cracking catalyst is contaminated during the catalytic cracking of a hydrocarbon feedstock, heavier than gasoline and containing nickel and vanadium poisons, in a cracking zone at an elevated temperature to produce gasoline, and nickel and vanadium are deposited on the catalyst, and the gasoline fraction produced by the cracking is treated with an aqueous sodium hydroxide solution which treatment produces waste caustic having a pH of about 7 to 12, the catalyst is cycled between the cracking zone and a regeneration zone to remove carbon by oxidation, and a portion of the catalyst is bled from the cracking system and subjected to a treatment which includes contacting substantially carbon-free catalyst with a molecular oxygen-containing gas at a temperature of about 1150 to about 1600° F., sulfiding the poisoning metal-containing component on the catalyst by contact with a sulfiding agent at a temperature of about 800 to 1500° F., chlorinating poisoning metal-containing component on the catalyst by contact with an essentially anhydrous chlorinating agent at a temperature of about 300 to 1000° F., removing poisoning metal chloride in vapor form from the catalyst, contacting the catalyst with a liquid, essentially aqueous medium to remove soluble, metal chloride from the catalyst, which treatment produces aqueous, acid-acting wastes; the improvement which comprises combining said acid-acting wastes from the catalyst treatment with an amount of said waste caustic from gasoline treating sufficient to neutralize the acid-acting wastes.

13. The method of claim 12 in which the sulfidation is effected by contact with H_2S, and the chlorination is effected by contact with an anhydrous chlorinating mixture comprising a chlorinating agent selected from the group consisting of HCl and Cl_2 and a promoter selected from the group consisting of chlorine-containing compounds of carbon and sulfur.

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