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(54) Immobilisation of vanadium deposited on sorbent materials during the treatment of oils containing heavy metals and coke precursors.

(57) Crude oils or residual fractions from the distillation of petroleum containing substantial amounts of metals such as Ni, V, Fe, Cu, Na and high Conradson carbon values are made suitable for processing in reduced crude conversion processes by preliminary contacting with a sorbent containing a metal additive to immobilize vanadium pentoxide deposited on the sorbent material.

It has been shown previously that as the vanadium pentoxide level builds up on the sorbent, the elevated temperature encountered in the regeneration zone causes the vanadia to flow and form a liquid coating on each particle. Any interuption of particle flow results in coalescence between the sorbent particles. Once coalescence occurs, fluidization becomes difficult to reinitiate. This results in stoppage of flow in the cyclone diplegs, ineffective operation of cyclones, rapid increase in loss of the sorbent, finally resulting in unit shutdown.

The sorbent can also be made, as we have done, by combining and precipitating other gels with the clay so as to act as a binder for initial utilization until some hydrothermal conditioning occurs. This binder, such as silica, alumina, titania, zirconia, calcia, boria, or magnesia then serves a dual purpose as disclosed herin.

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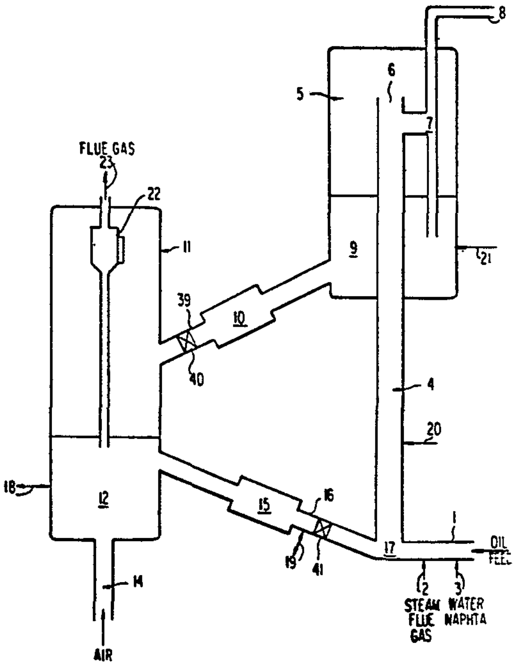


Metal additives, described in this invention, when properly applied serve to form compounds or complexes with vanadia which have melting points above the temperatures encountered in the regeneration zone, thus avoiding the formation of liquid vanadia and coalescence between particles. A second method of avoiding vanadia liquidation can be employed by means of select regeneration conditions wherein the regenerated sorbent is recovered in a partially coked state. In this case, the deposited vanadia is held in a lower oxidation state, the oxides of which have melting temperatures above those encountered in the regeneration zone.

BACKGROUND OF THE INVENTION

This invention is concerned with producing a high grade reduced crude having lowered metals and Conradson carbon values from a poor grade of reduced crude having extremely high metals and Conradson carbon values. In addition, this invention describes a sorbent material that can be utilized for the reduction of these metal and Conradson carbon values that exhibits a low catalytic cracking activity value. A further embodiment of this invention is the inclusion of a metal additive as a select metal, organo metallic, its oxide or salt into the sorbent material during manufacture or during the processing cycle to immobilize the sodium vanadate, vanadium pentoxide deposited on the sorbent during processing. This invention also describes a regeneration process to immobilize the vanadium pentoxide by maintaining the metal in a reduced or lower oxidation state to prevent vanadium mobility. This invention also provides a method for the processing of reduced crudes high in metals and Conradson carbon to provide a feedstock for a reduced crude conversion process or for typical fluid catalytic cracking processes.

The introduction of catalytic cracking to the petroleum industry in the 1930's constituted a major advance over previous techniques with the object to increase the yield of gasoline and its quality. These early FCC processes employed vacuum gas oils (VGO) from crude sources that were considered sweet and light. The terminology of sweet refers to low sulfur content and light refers to the amount of material boiling below approximately 1,000-1025°F. The catalyst employed in these early homogeneous dense beds were of amorphous siliceous materials, prepared synthetically or from naturally occurring materials activated by acid leaching. Tremendous strides were made in the 1950's in FCC technology as to metallurgy, processing equipment, regeneration and new more active amorphous catalysts. However, increasing demand with respect to quantity and increased octane number requirements to satisfy the new high horsepower-high compression engines being promoted by the auto industry, put extreme pressure on the petroleum industry to increase FCC capacity and severity of operation.

A major breakthrough in FCC catalysis which came in the early 1960's, was the introduction of molecular sieves or zeolites into the matrix of amorphous material constituting the FCC catalyst. These new zeolitic catalysts, containing a crystalline aluminosilicate in an amorphous matrix of silica, alumina, silica-alumina, clay, etc. were at least 1,000-10,000 times more active for cracking hydrocarbons than the earlier amorphous silica-alumina catalysts. This introduction of zeolitic cracking catalysts revolutionized the fluid catalytic cracking process. New innovations were developed to handle these high activities, such as riser cracking, shortened contact times, new regeneration processes, new and improved zeolitic catalyst developments, etc. The overall result (economic) of these zeolitic catalyst developments gave the petroleum industry the expensive, high pressure - special alloy multi-reactors system and a separate facility for the production of hydrogen and high operating costs.

To better understand the reasons why the industry has progressed along the processing schemes described, one must understand the effects of contaminant metals (Ni-V-Fe-Cu-Na) and Conradson carbon on the zeolitic containing cracking catalysts and the operating parameters of an FCC unit. High metal content, high Conradson carbon, high S, N, low H-content, high asphaltenes, and high boiling range are very effective restraints on the operation of a fluid cracking unit (FCC) or a reduced crude conversion unit (RCC) when seeking maximum conversion, selectivity and life. As these values increase, the capacity and efficiency of the FCC unit and RCC unit are adversely affected.

The effect of increasing Conradson carbon is to increase that portion of the feedstock converted to carbon deposited on the catalyst. In typical VGO operations employing a zeolite containing catalyst in a FCC unit the amount of coke deposited on the catalyst averages at about 4-5 wt% of feed. This coke production has been attributed to four different coking reactions, namely, contaminant coke (from metal deposits), catalytic coke (acid site cracking), entrained hydrocarbons (pore structure adsorption - poor stripping) and Conradson carbon. In the case of processing higher boiling fractions, e.g., reduced crudes, residual fractions, topped crude, etc., the coke production based on feed is the summation of three of the four kinds mentioned above plus exceedingly higher Conradson carbon values. Thus coke production when processing reduced crude is normally and most generally around 4-5 wt% plus the Conradson carbon value of the feedstock. In addition, it has been proposed that two other types of coke former processes or mechanisms may be manifested present in reduced crude processing in addition to the four exhibited by VGO. They are adsorbed and absorbed high boiling hydrocarbons not removed by normal efficient stripping due to their high boiling points, and carbon associated with high molecular weight nitrogen compounds adsorbed on the catalyst's acid sites.

The spent-coked catalyst is brought back to new equilibrium activity by burning off the deactivating coke in a regeneration zone in the presence of air and recycled back to the reaction zone. The heat generated during regeneration is removed by the catalyst and carried to the reaction zone for vaporization of the feed and to supply the heat for the cracking reaction. The temperature in the regenerator is limited because of metallurgy limitations and the thermal-steam stability of the catalyst. The thermal-steam stability of the zeolite containing catalyst is determined by the temperature and steam partial pressure at which the zeolite irreversibly loses its crystalline structure to form low activity amorphous material. Steam, generated by the burning of adsorbed carboneceous material containing a high hydrogen content is highly detrimental. This carboneceous material is principally hydrogen containing carboneceous product as previously described plus high boiling adsorbed hydrocarbons with boiling points as high as 1500-1700°F that have a high hydrogen content, high boiling nitrogen containing hydrocarbons and porphyrins-asphaltenes.

It has also been shown that zeolite containing catalysts are also very sensitive to vanadia. Small amounts of vanadia seem to catalyze the distruction of crystalline zeolites.

As the Conradson carbon value of the feedstock increases, coke production increases and this increased load will raise regeneration temperatures; thus the unit is limited as to the amount of feed and Conradson carbon values it can process. Earlier VGO units operated with the regenerator at 1150-1250°F. New developments in reduced crude processing such as Ashland Oil's "Reduced Crude Conversion Process" (pending application USSN 094,216) can operate up to 1350-1450°F. But at adiabatic conditions, even these higher temperatures place a limit on the Conradson carbon value of the feed which can be tolerated at approximately about 8. Based on experience, this equates to about 12-13 wt% coke on catalyst based on feed.

The metal containing fractions of reduced crude contain Ni-V-Fe-Cu, present as porphyrins and asphaltenes. These metal containing hydrocarbons are deposited on the catalyst during processing, are cracked in the riser to deposit the metal or carried over by the spent catalyst as the metallo-porphyrins or asphaltenes and converted to the oxide during regeneration. The adverse effects of these metals are to decrease the acidity of the zeolite therby reducing catalytic cracking activity, thus, enhancing non-selective cracking and dehydrogenation to produce light gases such as hydrogen, methane and ethane and more importantly, increase coke production all of which affects selectivity and yield. The increased production of light gases affects the economic yield and selectivity structure of the process and puts an increased demand on compressor capacity. The increase in coke production also adversely affects catalyst activity-selectivity and leads to increased regenerator air demand and compressor capacity, and elevated regenerator temperatures.

These problems of the prior art were solved by the development of the Reduced Crude Conversion Process, see pending applications 094,216 and 094,092. This new process can handle reduced crudes containing high metals and Conradson carbon values. However, certain crudes such as Mexican Mayan or Venezuelan which contain abnormally high metal and Conradson carbon values if processed in a reduced crude process will lead to an uneconomical operation because of the high load on the regenerator and the high catalyst addition rate required to maintain catalyst activity and selectivity. The addition rate can be as high as 4-8 lbs/bbl. which at today's catalyst prices can add as much as $2-8/bbl additional catalyst cost to the processing economics. On the other hand, it becomes economically desirable that an economical means be developed to process crude oils such as the Mexican Mayan because of their availability and cheapness as compared to Middle East crudes.

It was noted in the literature that a process was developed by Engelhard Minerals and Chemicals which seeks to reduce the metal content and Conradson carbon of these crudes. The process is described in U. S. Patent 4,243,514 and German Patent No. 29 04 230. Basically, this process involves contacting a reduced crude fraction with sorbent at elevated temperature in a fluid bed of the RCC type, to produce a product of reduced metal and Conradson carbon value. The claimed preferred sorbent is an inert solid initially composed of kaolin, which has been spray dried to yield a microspherical particle having a surface area below 100 m^2/g a catalytic cracking micro-activity value of less than 20 and calcined at high temperature so as to achieve attrition resistance. This process was experimentally tested and found to lower the metals and Conradson carbon values substantially. However, as the vanadia content on the sorbent increased, in the range of 10,000-30,000 ppm, the sorbent began to have fluidization problems apparently due to the clumping, fusion or coalescence of particles. This could only be overcome by the removal of spent sorbent and the addition of fresh virgin material.

SUMMARY OF THE INVENTION

The problems of the prior art are now overcome in a process employing the sorbent and metal additive of this invention which allows the processing of a reduced crude or crude oil of extremely high metals and Conradson carbon values.

A reduced crude or crude oil having a high metal and Conradson carbon value is contacted in an RCC type regenerator-reactor system with an inert solid sorbent of low surface area at temperatures above about 900°F. Residence time in the riser is below 5 seconds, preferably 0.5-2 seconds. The particle size of the inert solid sorbent is approximately 20-150 microns in size to ensure adequate fluidization properties.

The reduced crude-crude oil is introduced at a temperature below thermal cracking at the bottom of the riser and contacts the inert solid sorbent at a temperture of 1150-1400°F and exits the riser at a temperature in the reactor vessel of approximately 900-1050°F. Along with reduced crude or crude oil; water, steam, naphtha, flue gas, etc. may be introduced to aid in vaporization and act as a lift gas to control residence time. The sorbent is rapidly separated from the hydrocarbon vapors at the top of the riser by employing the vented riser concept developed by Ashland Oil, Inc., see U. S. Patent No. 4,066,533. During the course of the reaction in the riser the metal and Conradson carbon compounds are deposited on the sorbent. After separation in the vented riser the spent sorbent is deposited as a dense bed at the bottom of the reactor vessel, transferred to a stripper and then to the regeneration zone. The spent sorbent is contacted with an oxygen containing gas to remove the carboneceous material through combustion to carbon oxides to yield a regenerated sorbent containing 0.05-0.2 wt% carbon. The regenerated sorbent is then recycled to the bottom of the riser to meet additional high metal and Conradson carbon containing feed to repeat the cycle.

At the elevated temperatures encountered in the regeneration zone, the vanadium deposited on the sorbent is converted to vanadium oxides, in particular, vanadium pentoxide. The melting point of vanadium pentoxide is much lower than temperatures encountered in the regeneration zone. Thus it can become mobile, flow across the sorbent surface, cause pore plugging, partial particle fusion, increase in particle density, and decrease the fluidization properties of the sorbent. In addition, and more importantly, in this application, any momentary stoppage of flow, such as occurs in a cyclone dipleg, permits coalescence of two or more particles and ultimately inhibition of flow and loss of cyclone operation. Further, when the unit is brought down to low temperatures to clear the system, the vanadium pentoxide solidifies, thus causing solid plugs of microspheres bound together by the vanadium pentoxide cement. This cause and effect of vanadium pentoxide can be overcome by two methods.

We now have found that 1) The incorporation of select metals, metal oxides or their salts into the sorbent during manufacture, impregnation after spray drying or added during processing at select points in the units to affect compound or complex formation. These compounds or complexes of vanadia with the metal additives have higher melting points than the temperatures encountered in the regeneration zone. 2) Utilization of select regeneration conditions to ensure that not all of the carbon is removed from the sorbent surface thus ensuring a reducing atmosphere and the resulting in the maintenance of vanadia in lower oxides or oxidation states of vanadium all of which are extremely high melting solids, e.g., the lower oxides of vanadium melt above the regenerator temperature encountered and contemplated.

The process of this invention and sorbent are not limited to a fluidized bed operation with microspherical particles of 10-200 microns in size, but can include moving bed operations employing microspherical particles of greater than 200 microns in size.

DESCRIPTION OF PREFERRED EMBODIMENTS

The select sorbents of this invention will include solids of low catalytic activity, such as spent catalyst, clays, bentonite, kaolin, montmorillonte, smectites, and other 2-layered lamellar silicates, mullite, pumice, silica, laterite, etc. The surface area of these sorbents would preferably be below 25 m^2/g, have a pore volume of approxmately 0.2 cc/g or greater and a micro-activity value as measured by the ASTM Test Method No. D3907-80 of below 20.

To an aqueous slurry of the raw sorbent is mixed the metal additive to yield approximately 1-6 wt% concentration on the finished sorbent. The metal additive is a water soluble compound which can be the oxide or one of its salts such as the nitrate, halide, sulfate, carbonate, etc. This mixture is spray dried to yield the finished promoted sorbent as a microspherical particle of 10-200 microns in size with the active promoter deposited within the pores and/or the outer surface of the sorbent particle. Since the concentration of vanadia on the spent sorbent is targeted to be approximately 2-5 wt% of final particle weight, the concentration of metal additive will be in the range of 1-6 wt% to maintain at least a one to one atomic ratio of vanadium to metal additive at all times. The sorbent can also be impregnated with these metal additives after spray drying, employing techniques well known in the art or combined with the clay as a gel so as to serve also as a binder and pore volume extender in the spray dried product.

It is not proposed to define the exact mechanism for the immobilization of vanadia but the metal additives of this invention will form compounds or complexes with vanadia that have higher melting points or serve to immobilize the migration of vanadia at the temperatures encountered in the regeneration zone. The targeted one to one molar ratio is chosen as more or less a practical objective. Initially, in those cases where the additive is included in the preparation the metal additive will be at a concentration far exceeding targeted ratios. However, as vanadia content increases, this ratio gradually decreases as vanadia is deposited on the sorbent. The melting point and migration behavior of the vanadia-metal oxide compound or complex decreases, as vanadia increases, usually approaching a eutectic having a melting point even lower than vanadium pentoxide. For this reason, the additive is kept high in the virgin sorbent or is added in approximately stoichiometric proportions with vanadium in the feedstock.

Although described in the literature, one to one by weight preparations (50 wt% vanadium pentoxide - 50 wt% additive metal) were made and the melting points of the binary mixtures determined by differential thermal analyses (DTA). This strategy was employed to determine suitable metals-metal oxides combinations which can form binary mixtures with vanadium pentoxide having melting points of at least 1800°F at this approximate one to one ratio. Relatively high melting point tends to ensure that particle fusion does not occur at the regeneration temperature. The metal-metal oxides additive would include the following groups and their active elements from the Periodic chart of the elements:

		M.P. of 1/1 Mixture - °F
Group IIA	Mg, Ca, Sr, Ba	1740-1900
Group IIIB	Sc, Y, La	1800-2100
Group IVB	Ti, Zr, Hf	1700-2000
Group VB	Nb, Ta	1800-2000
Group VIIB	Mn	1750
Group VIII	Fe, Co, Ni	1600-1800
Group IIIA	In, Tl	1800
Group VA	Bi	1800
Group VIA	Te	1500
Lanthanide Series	Ce, Pr, etc.	2100
Actinide Series	Th, U, etc.	-

Because of cost, and other factors only a select few of the above are considered practical. These would include Mg, Ca, Ba and titanium and iron oxide. The reaction of the metal additive with vanadia frequently yields a binary compound. This invention also recognizes that heating mixtures of these additive metals with vanadia can also cause reactions to occur to form more complex compounds, and that combinations of two or more of these metal additives with vanadia can also yield even more unusual compounds and combinations thereof. In addition, ternary and quaternary combinations can occur with metals not covered in the Groups illustrated above. In these discussions we have covered vanadia and vanadium pentoxide. However, this approach also relates to the lower valences of vanadium, and further, in processing a sulfur containing feed and regeneration in the presence of an oxygen containing gas there will likely exist vanadium sulfides, sulfites, sulfates, and which will create still other mixtures containing mixed oxides and sulfides, sulfates, etc.

If the metal additive is not incorporated in the initial sorbent preparation or added to the sorbent during manufacture then it can be added during the processing cycle at any point of sorbent travel in the processing unit. This would include but not be limited to addition of an aqueous solution of the inorganic metal salt or hydrocarbon solution of metallo-organic compounds at the riser bottom 17, along the riser length 4, the dense bed 9 in reactor vessel 5, stripper 10 and stripper 15, regenerator inlet 14, regenerator dense bed 12, or regenerated sorbent standpipe 16.

In another embodiment, the vanadium deposited on the sorbent is immobilized through select regeneration conditions. Initially, the vanadium is deposited on the sorbent and in the regeneration zone under typical conditions is converted to vanadium pentoxide during coke combustion. The sorbent containing vanadium pentoxide is transferred to the riser and under the reducing conditions resulting from contacting vaporized feed will undergo reduction to lower oxidation states. Since reduced vanadium oxide is covered by the heavy coke deposition it will be protected against oxidation in the regeneration zone. Under controlled conditions of combustion the coke level on the sorbent will be reduced to 0.05-0.2 wt% on sorbent weight, preferably 0.1-0.2 wt%. Operation of the regenerator in a semi-reducing condition, namely high CO/CO_2 ratio can also be utilized to maintain vandium in a lower valence state. This type of operation establishes a condition wherein all the oxygen has been consumed and that none is left to further reduce the coke level or oxidize the vanadium to a higher oxidation level. Thus the reduction of vanadium pentoxide in the riser yields vanadium oxide (V^{+4}, VO_2) and vanadium trioxide (V^{+3}, V_2O_3) which have much higher melting points, such as 1800°F or higher. Under these controlled regeneration conditions the lower vanadium oxidation states are maintained so as to avoid the flow and fusion problems which otherwise would occur.

The selective sorbent of this invention with or without the additive metal promoter is charged to a fluidized Metal Removal System as outlined in Figure 1. Sorbent particle circulation and operating parameters are maintained by methods well known to those skilled in the art. The equilibrium sorbent at temperatures of 1100-1400°F contacts the reduced crude containing high metals and Conradson carbon values at riser wye 17. The reduced crude can be accompanied by steam and/or naphtha, or dry gases or flue gas injected at point 2, water and/or naphtha injected at point 3 to aid in vaporization, sorbent fluidization and controlling contact time in riser 4. The sorbent and vaporous hydrocarbons travel up riser 4 at a contact time of 0.1-5 seconds, preferably 0.5-2 seconds. The sorbent and vaporous hydrocarbons are separated in vented riser outlet 6 at a final reaction temperature of 900-1050°F. The vaporous hydrocarbons are transferred to cyclone 7 where any entrained sorbent fines are separated and the hydrocarbon vapors are sent to the fractionator via transfer line 8. The spent sorbent drops to the bottom of vessel 5 to form a dense bed 9. The spent sorbent is then transferred to stripper 10 for removal of any entrained hydrocarbon vapors and then to regenerator vessel 11 to form dense bed 12. An oxygen containing gas such as air is admitted to the bottom of dense bed 12 in vessel 11 to combust the coke to carbon oxides. The resulting flue gas is processed through cyclones and exits from regenerator vessel 11 via line 13. The regenerated sorbent is transferred to stripper 15 to remove any entrained combustion gases and then transferred to riser wye 17 via line 16 to repeat the cycle.

At such time that the metals level on the sorbent becomes higher such that demetallization and decarbonization of the reduced crude feedstock declines, additional sorbent can be added and inactive sorbent withdrawn at addition-withdrawal point 18 into dense bed 12 and at addition withdrawal point 19 into regenerated sorbent standpipe 16. Addition points 18 and 19 can be utilized to add a metal additive promoted sorbent. In the case of a non-promoted sorbent, the metal additive as an aqueous solution or an organo-metallic compound in aqueous or hydrocarbon solvent can be added at addition points 18 and 19 as well as at addition points 2 and 3 on feed line 1, addition point 20 in riser 4, addition point 21 to the bottom of vessel 5 into dense bed 9. The addition of the metal additive is not limited to these locations but can be practiced at any point along the reduced crude-sorbent processing cycle.

At such time that the metal promoted sorbent is not utilized than vanadia deposited on the sorbent is immobilized through the use of the select regeneration conditions described earlier in this invention. Sorbent and reduced crude feedstock are processed in a manner similar to that described previously. The spent sorbent after stripping in stripper 10 is transferred to regenerator vessel 11. The amount of oxygen containing gases admitted though line 14 into dense bed 12 is sufficient to only regenerate a large portion of the coke deposited on the sorbent. The regenerated sorbent exiting regenerator vessel 11 to stripper 15 contains 0.05-0.2 wt% coke, preferably 0.1-0.2 wt%. This amount of coke on regenerated sorbent is sufficient to help ensure that the vanadium pentoxide reduced in the riser to lower vandium oxides (monoxide, trioxide) will remain in these reduced states. The small amount of coke remaining on the sorbent ensures that vanadium in the lower oxidation state is not re-oxidized to the higher +5 state.

The regenerator vessel as illustrated in Figure 1 is a simple one zone-dense bed type. The regenerator section is not limited to this example but can exist of two or more zones, stacked or side-by side arrangement, with internal and/or external circulation transfer lines from zone to zone.

Having thus described the sorbent, metal additive promoters and process of this invention, the following examples are provided to illustrate the effect of vandadia flowing and causing particle coalescence which affect the fluidization properties and the steps taken to better understand this process and prevent its occurrence.

EXAMPLES

The determination that vanadia deposited on a sorbent would flow and cause coalescence between the sorbent particles at regenerator temperatures and what elements and their salts would prevent this processs were studied by three methods; namely, the clumping or lump formation technique, vanadia diffusion from or compound formation with a metal additive in a alumina-ceramic crucible, and through spectroscopic studies and differential thermal analyses of vanadia-metal additive mixtures.

CLUMPING TEST

A sorbent clay, spray dried to yield microspherical particles in 20-150 micron size, had vanadia deposited upon it in varying concentrations. The sorbent, free of vanadia, and those containing varying vanadia concentrations were placed in individual ceramic crucibles and calcined at 1400°F in air for two hours. At the end of this time period the crucibles were withdrawn from the muffle furnace and cooled to room temperature. The surface texture and flow characteristics of these samples were noted and the results are reported in Table I.

TABLE I

V_2O_5 Concentration - ppm	Surface Texture	Flow Characteristics
0	Free	Free flowing
1,000-5,000	Surface Clumped	Broke crust-free flowing
5,000-20,000	Surface Clumped	Total clumping-no flow

As shown in Table I, the sorbent free of vanadia does not form any crust or clumps or fused particles at temperatures encountered in the regenerator section of the process described in this invention. At vanadia concentrations above 5,000 ppm the absorbent begins to clump and bind badly and does not flow at all.

While liquid at operating temperatures, manifestation of this phenomenum is demonstrated by the finding which occurs when these samples are cooled down below the solidification point in a crucible, or the operating unit is cooled down in order to facilitate entrance to the unit for cleaning out plugged diplegs and other repairs. This phenomenum also makes a turnaround extremely difficult, as this material must be chipped out.

CRUCIBLE DIFFUSION - COMPOUND FORMATION

An extension of the clumping test is the use of a ceramic-alumina crucible to determine the end product of vanadia reacting with the metal additives. If vanadia does not react with the metal additive or only a small amount of compound formation occurs, then the vanadia will diffuse through and over the porous alumina walls and deposit as a yellowish to orange deposit on the outside walls of the crucible. On the other hand, when compound formation occurs, there is little or no vanadia deposits on the outside crucible wall. Two series of tests were performed, in the first series shown in Table 2, 1/1 mixture by weight of vanadia pentoxide and the metal additive was placed in the crucible and heated to 1500°F in air for 12 hours. Compound formation or vanadia diffusion was noted.

TABLE II

1 Part V_2O_5 + 1 Part Metal Additive

1500°F - Air - 12 Hours

Metal Additive	Diffusion of Vanadium	Compound Formation
Titania	No	Yes
Manganese Acetate	No	Yes
Lanthanum Oxide	No	Yes
Alumina	Yes	No
Barium Acetate	No	Yes
Copper Oxide	Yes	Partial

In the second series of tests a vanadia containing sorbent was tested in a similar manner. A one to one ratio by weight of the vanadia containing sorbent and the metal additive were heated to 1500°F in air for 12 hours. The results are shown in Table III.

TABLE III

1 Part V_2O_5 - Sorbent + 1 Part Metal Additive

1500°F - Air - 12 Hours

Vanadia Concentration, ppm	Metal Additive	Particle Coalescence
24,000	None	Yes
24,000	Vanadia addition	Yes
24,000	Calcium Oxide	No
24,000	Magnesium Oxide	No
24,000	Manganese Oxide	No

The study on the capability of certain elements to form higher melting compounds with vanadium pentoxide was extended to DuPont differential thermal analyses (DTA), X-ray diffraction (XRD) and scanning electron microscope (SEM) instruments. The metal additives studied on the DTA showed that titania, barium oxide, calcium oxide, iron oxide and indium oxide were excellent additives for the formation of high melting metal vanadates, melting points of 1800°F or higher. Copper and manganese gave intermediate results with compounds melting at approximately 1500°F. Poor results were obtained with materials such as lead oxide, molybdena, tin oxide, chromia, zinc oxide, cobalt oxide, cadimium oxide and some of the rare earths.

The material reported and produced in Table 3, namely 24,000 ppm vanadia on sorbent with no metal additive, was fired at 1500°F and then studied in the SEM. The fused particles initially gave a picture of fused particles, however, as the material was continuously bombarded the fused particles separated due to the heat generated by the bombarding electrons. One was able to notice the melting and flowing of vanadia with the initial single fused particles separating into two distinct microspherical particles.

An example of our XRD work is the identification of the compound formed when manganese acetate reacted with vanadium pentoxide. This compound has been tentatively identified as $Mn_2V_2O_7$.

The commercial application of the metal additive of this invention is illustrated in Figure 2. As shown in November a reduced crude was processed over a virgin sorbent and after 10,000 ppm vanadia the catalyst began to exhibit extreme clumping properties. This was repeated in December. In January, the metal additive was added to the reduced crude and reduced its clumping properties. The additive was DuPont's Tyzor TPT (tetraisopropyl titanate).

We Claim,

1. A process for preparing a reduced crude or crude oil of reduced metal and Conradson carbon content from a reduced crude or crude oil having a substantial metal and Conradson carbon content, the improvement of which comprises contacting said feedstock with a metal additive promoted sorbent to immobilize vanadium compounds, said sorbent having a catalytic cracking micro-activity test value of less than 20, at elevated temperatures in a riser fluidized transfer zone or moving bed reaction zone followed by rapid separation of the gaseous products and spent sorbent, subjecting said spent sorbent to regeneration in the presence of an oxygen containing gas, with recycle of the regenerated sorbent to the riser transfer zone or moving bed reaction zone for treatment of fresh reduced crude or crude oil.

2. The process of Claim 1 wherein the reduced crude or crude oil contains 100 ppm or more of metals consisting of nickel, vanadium, iron and copper and the Conradson carbon value is 8 wt% or higher and wherein the product after decarbonization and demetallization contains less than 100 ppm metals, preferably less that 50 ppm metals and less than 10 wt% Conradson carbon, preferably less than 8 wt% Conradson carbon and wherein said sorbent is in microspherical form, prepared from a hydrated clay and has a surface area below about 50 m^2/g and a pore volume of 0.2 cc/g or greater.

3. The process of Claim 1 wherein the vanadium concentration on the sorbent is 10,000 ppm or greater and wherein the metal additive to immo-

bilize vanadium compounds on a sorbent will include the following elements: Mg, Ca, Sr, Ba, Sc, Y, La, Ti, Zr, Hf, Nb, Ta, Mn, Fe, In, Tl, Bi, Te, lanthanide and actinide series of elements.

4. The process of Claim 1 wherein the product from the decarbonization-demetallization process is utilized as feedstock for a reduced crude conversion process of fluid catalytic cracking process.

5. A process for preparing a reduced crude or crude oil of reduced metal and Conradson carbon content from a reduced crude or crude oil having a substantial metal and Conradson carbon content, the improvement of which comprises contacting said feedstock with a sorbent having a catalytic cracking micro-activity test value of less than 20, at elevated temperatures in a riser fluidized transfer zone or moving bed reaction zone followed by rapid separation of the gaseous products and spent sorbent, subjecting said spent sorbent to controlled regeneration conditions to immobilize the vanadium compounds deposited on the sorbent, in the presence of an oxygen containing gas to yield a partially regenerated sorbent and the deposited vanadium in the lower oxidation state, with recycle of the regenerated sorbent to the riser transfer zone or moving the reaction zone for treatment of fresh reduced crude or crude oil.

6. The process of Claim 5 wherein the reduced crude or crude oil contains 100 ppm or more of metals consisting of nickel, vanadium, iron and copper and the Conreadons carbon value is 8 wt% or higher and

wherein the product after decarbonization and demetallization contains less than 100 ppm metals, preferably less than 50 ppm metals and less than 10 wt% Conradson carbon, preferably less than 8 wt% Conradson carbon.

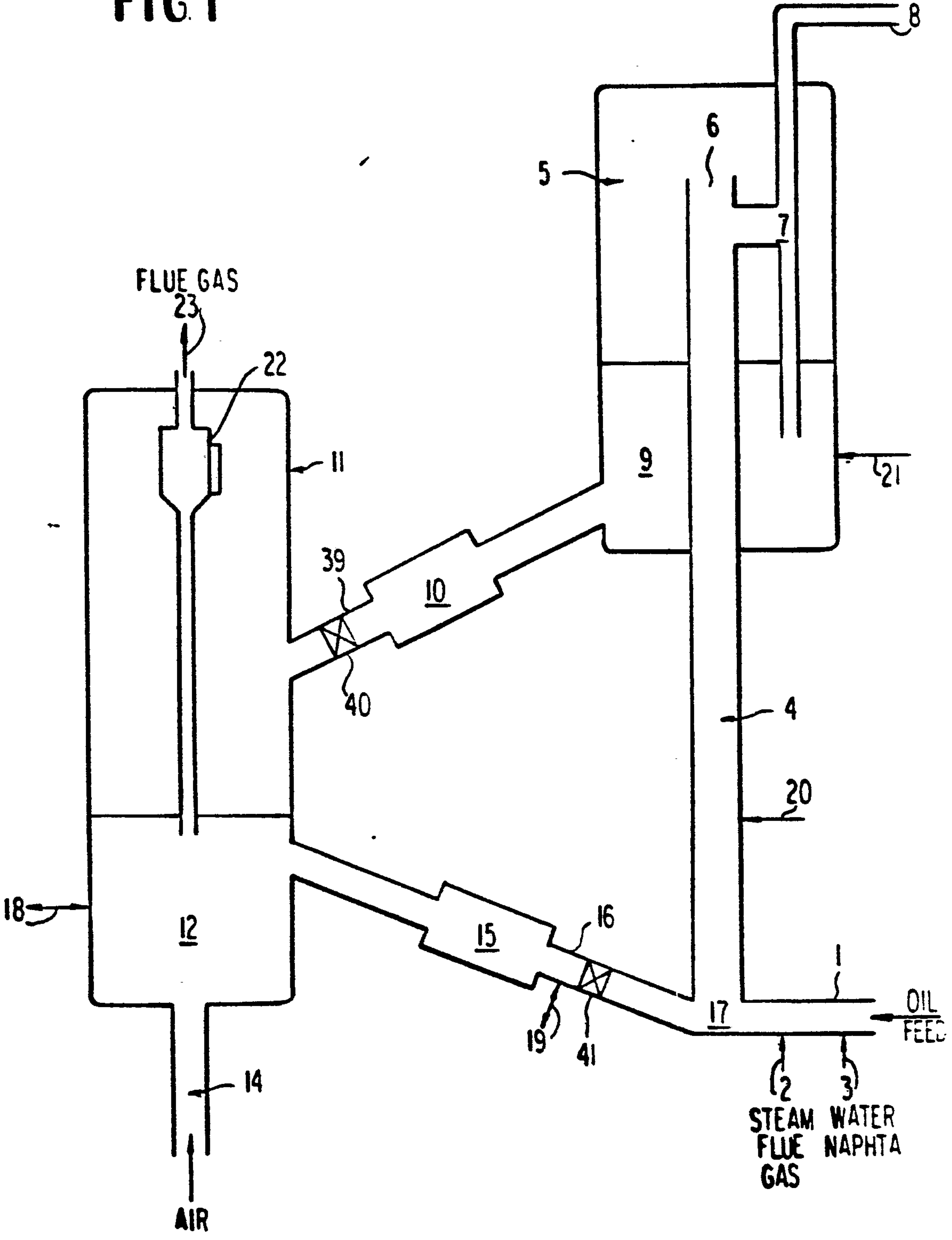
7. The process of Claim 5 wherein the vanadia oxidation state is reduced to a lower level in the riser transfer reaction zone and maintained at this lower level by employing incomplete combustion of the coke on the sorbent in the regeneration zone.

8. The process of Claim 5 wherein the sorbent is prepared from clays, bentonite, kaolin, montmorillonites, smectites and other 2-layered lamellor silicates, mullite, pumice, silica, laternite and wherein binder materials would be added to the sorbent which include Mg, Ca, Ba, Ti, Zr, Ta, In, Bi, and Fe.

9. The composition of matter is use in process Claim 1 and Claim 5 containing microspherical clay and 1-6 wt% titanium or zirconium as an oxide in final form.

10. The composition of matter is use in process Claim 1 and Claim 5 containing microspherical clay and 1-6 wt% tantalum, bismuth, or indium as an oxide in final form.

FIG I



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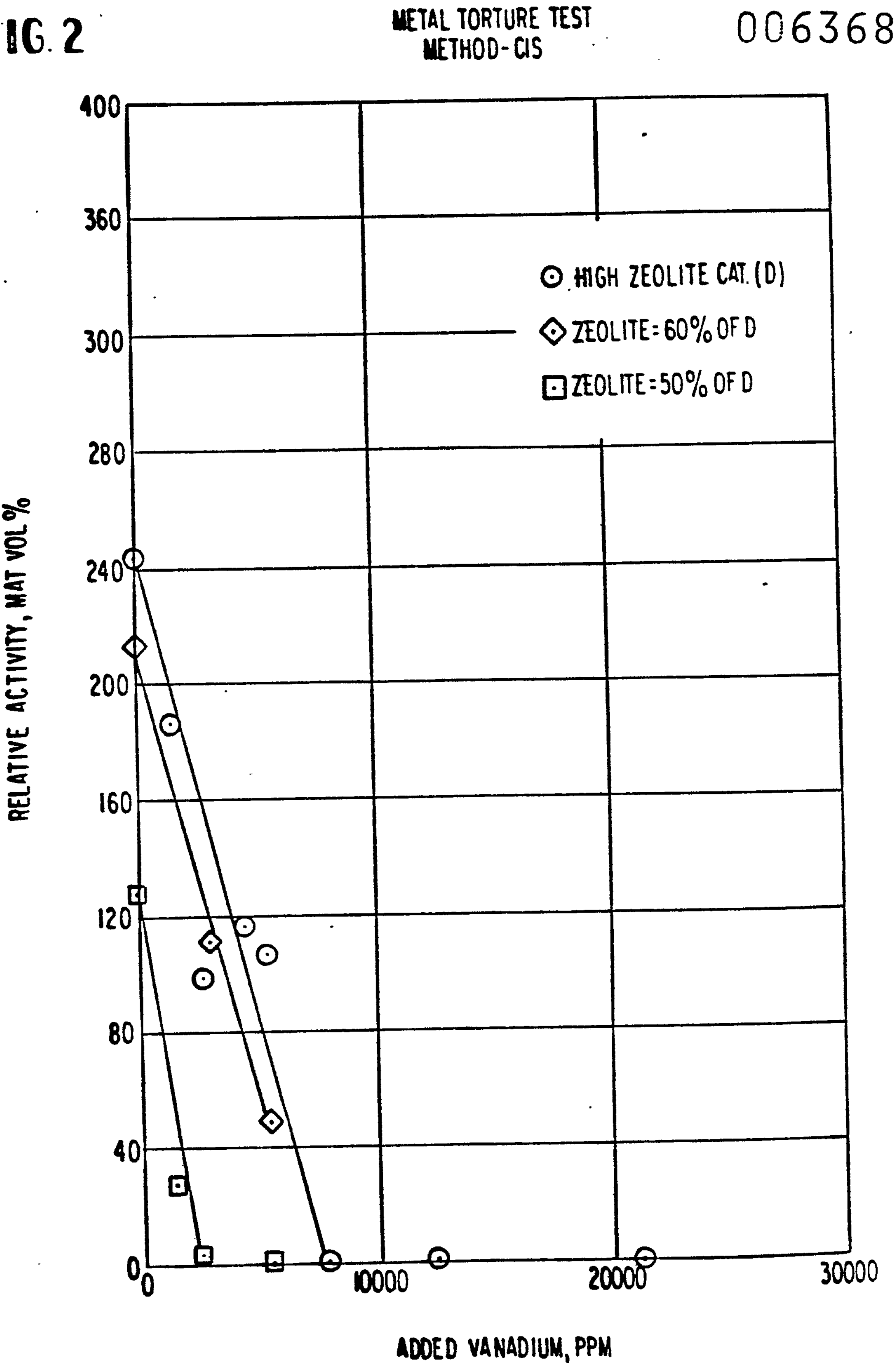
IG. 2


METAL TORTURE TEST
METHOD-CIS
RELATIVE ACTIVITY, MAT VOL %
ADDED VANADIUM, PPM
0
40
80
120
160
200
240
280
300
360
400
0
10000
20000
30000
⊙ HIGH ZEOLITE CAT. (D)
◇ ZEOLITE = 60% OF D
⊡ ZEOLITE = 50% OF D

IG 3

METAL TORTURE TEST
METHOD - CIS

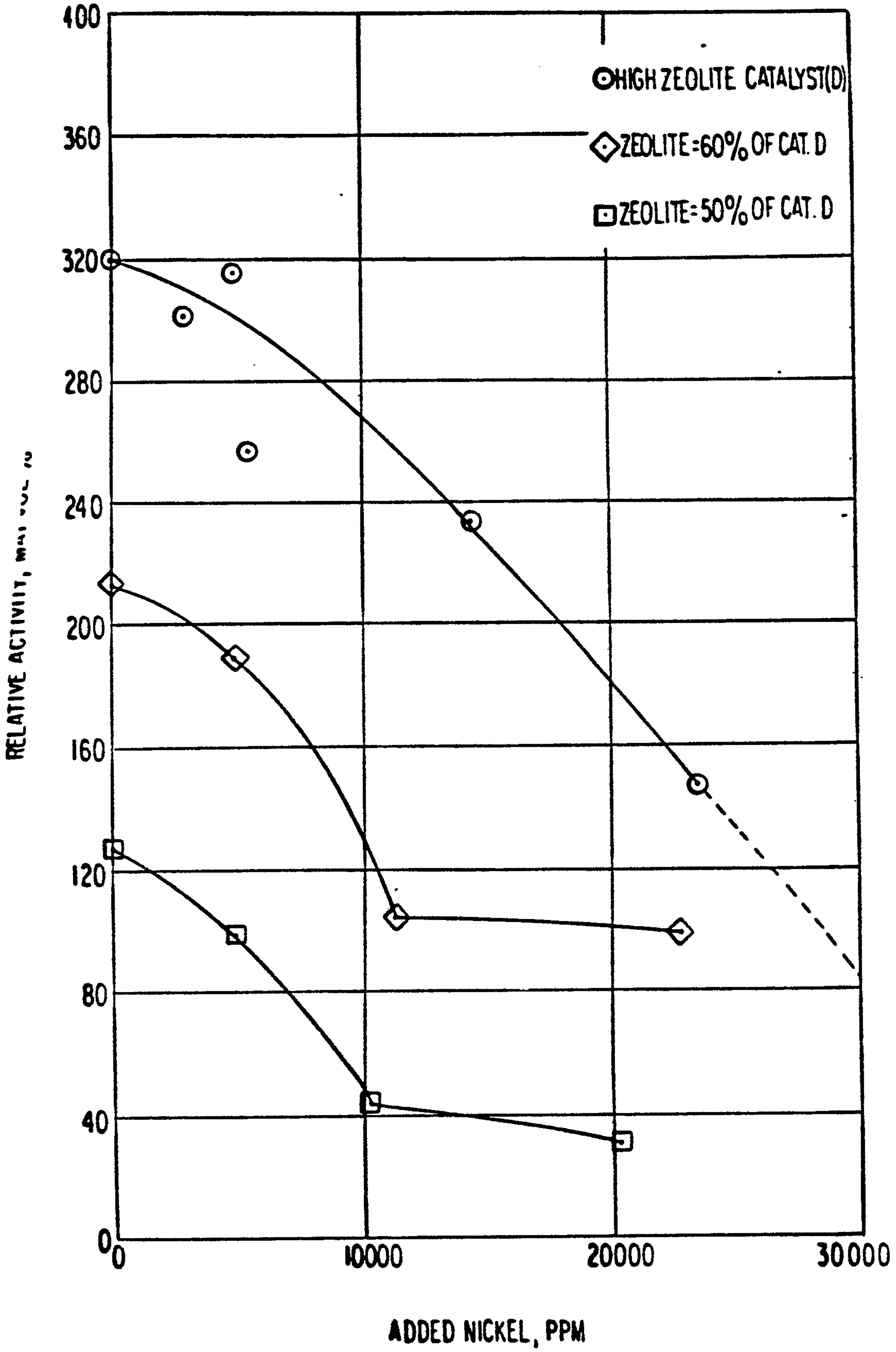


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FIG. 4

METAL TORTURE TEST
METHOD - CIS
VANADIUM EFFECTS

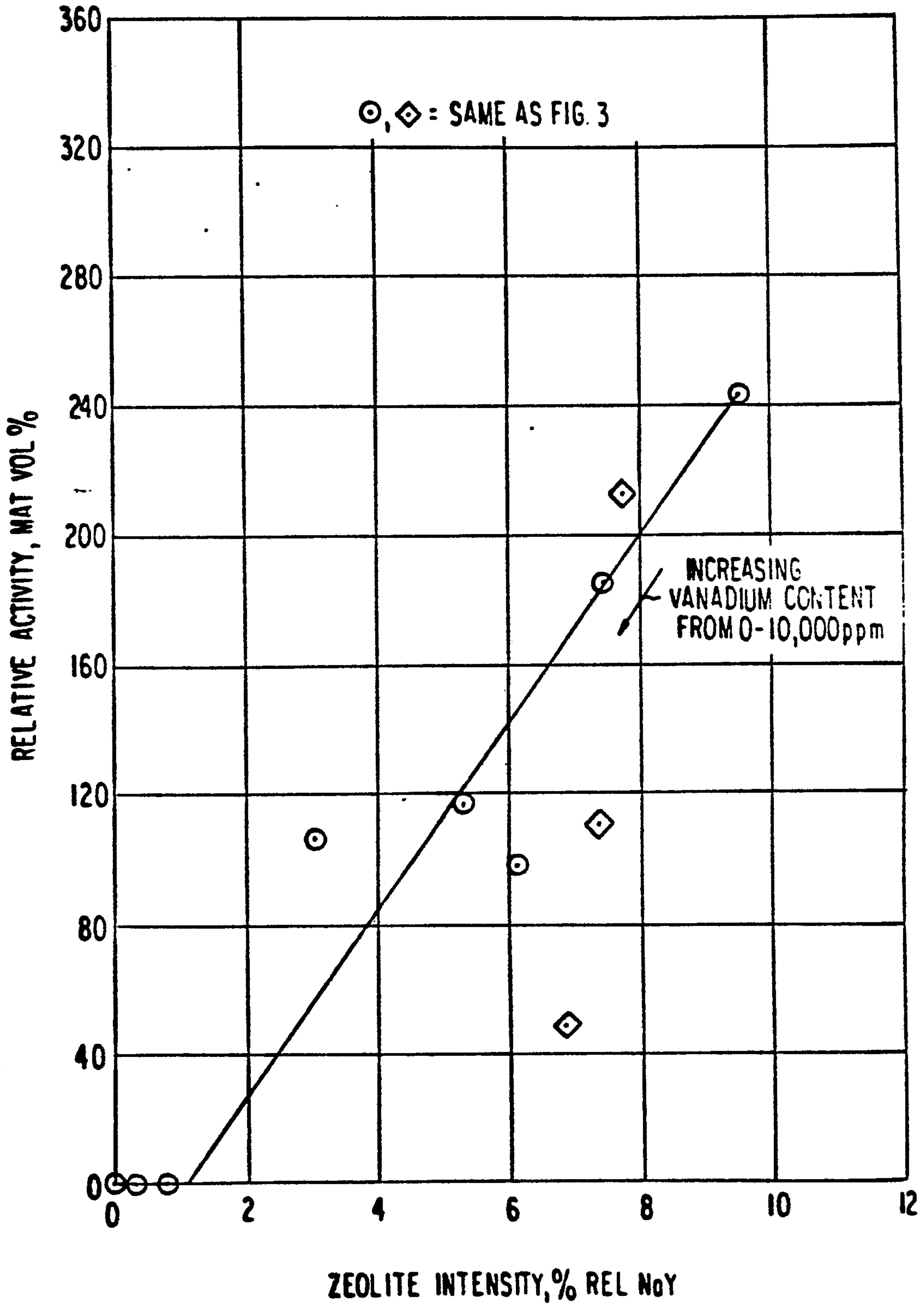

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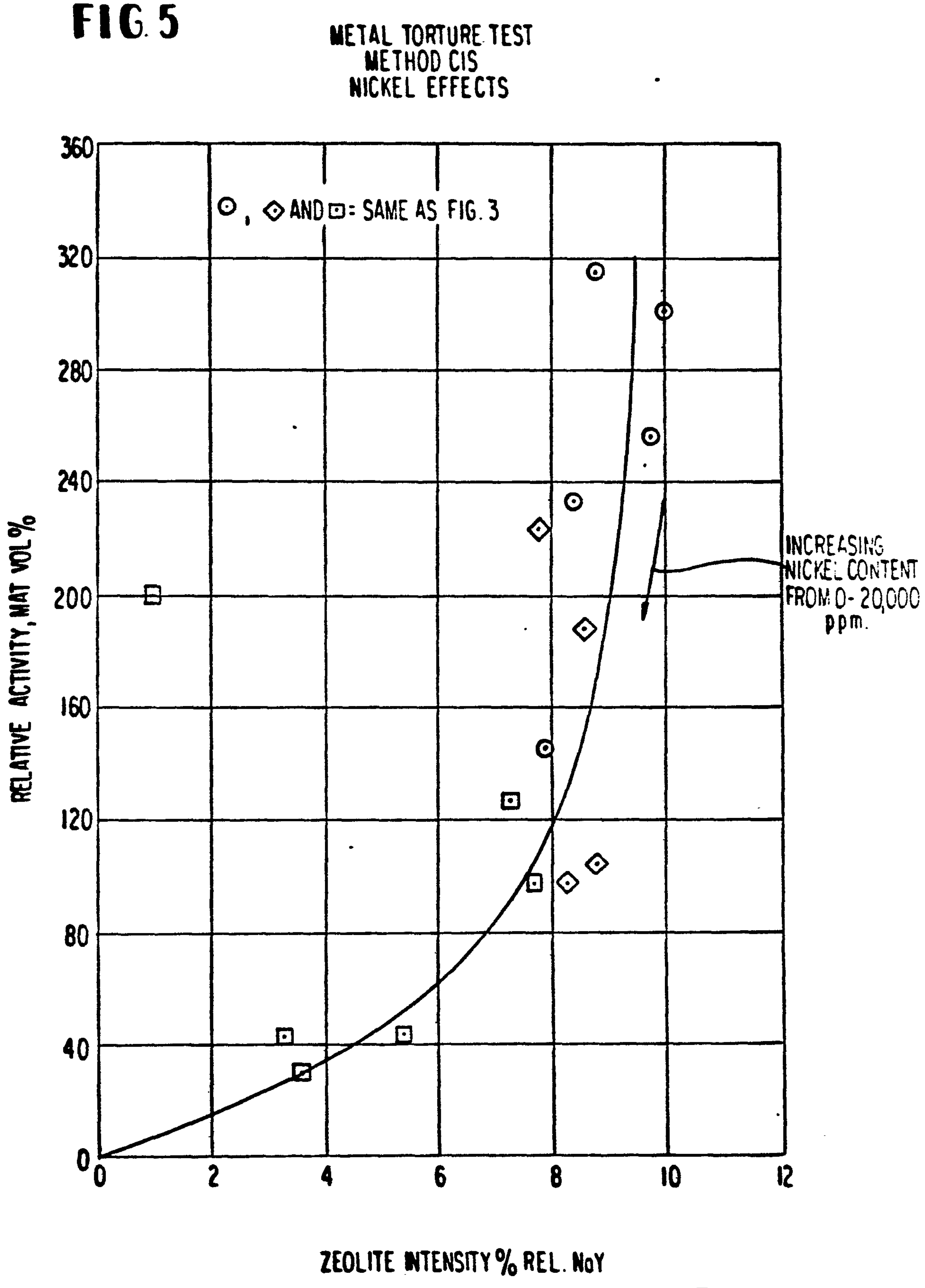
FIG. 5



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METAL TOLERANCE
TORTURE TEST METHOD/3-CIS

SAMPLE NO.	ADDED METAL TYPE	WT % IB	SURFACE ARE m²/g	ZEOLITE % NaY	MAT DATA							
					REL. ACT.	CONV. VOL.%	CONV. WT%	GAS WT%	COKE WT%	GASO. WT%	CPF	HPF
B600-159												
1	Ni	0.48	115	7.7	98	74.8	73.4	16.6	7.1	49.6	2.5	17.0
2	Ni	1.06	77	3.3	74	72	65.4	15.6	3.8	45.9	1.4	12.1
3	Ni	2.06	66	3.6	55	70	62.1	13.5	3.0	45.6	1.3	15.1
4	V	0.14	55	4.4	52	69	65.2	16.7	1.2	47.3	0.5	2.0
5	V	0.24	35	2.2	8	52	49.9	12.2	0.5	37.2	0.4	2.5
6	V	0.61	11	0.0	0	2	12.2	5.0	0.2	7.0	0.8	7.1
19	V	1.79	11	0.0	0	3	9.5	5.2	0.4	3.9	1.4	10.3
21	CONTROL		73	5.4	44	68					0.9	0.4
	CONTROL		84	7.3	127	77	73.0	16.0	2.9	55.0	0.9	0.8

FIG 6

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FIG. 7

METAL TOLERANCE
TORTURE TEST METHOD/3-CIS

SAMPLE NO.	ADDED METAL TYPE WT % IB	SURFACE AREA m2/g	ZEOLITE % NaY	MAT DATA REL. ACT.	CONV. VOL.%	CONV. WT%	GAS WT%	COKE WT%	GASO. WT%	CPF	HPF
B600-159-											
10	Ni 0.49	240	8.6	456	88	78.3	17.6	5.7	55.0	1.3	11.5
11	Ni 1.13	239	8.8	188	81	75.0	19.2	4.9	50.8	1.5	13.8
12	Ni 2.27	219	8.3	186	81	74.4	16.9	7.2	50.2	2.1	28.0
13	V 0.13	238	8.1	341	86	80.5	22.6	3.6	54.3	0.9	2.7
14	V 0.34	213	7.4	192	81	75.5	20.4	3.0	52.0	0.9	9.7
15	V 0.55	211	6.9	97	74.7	68.7	15.2	4.6	490	1.7	16.6
20	V 1.11	159	3.5	27	63	58.4	11.8	4.6	42.0	2.3	31.9
22	CONTROL	143	4.8								
	CONTROL	242	7.8	213	82	80.0	21.6	4.8	53.6	1.3	1.3

FIG. 8

STEAMING PERFORMED AT 1450°F - 5 HRS.
V AS VANADIUM NAPHTHENATE Ti AS
TRIPROPYLTITANATE

STANDARD CATALYST RUN #	V ppm	Ti ppm	Ti ADDITION	ZEOLITE INTENSITY
1	0	0	-	9.4
2	5500	0	-	3.1
3	5500	5500	Ti ADDED AFTER V REGENERATION	3.5
4	5500	5500	Ti ADDED WITH V COMPOUND THEN REGENERATED	8.2

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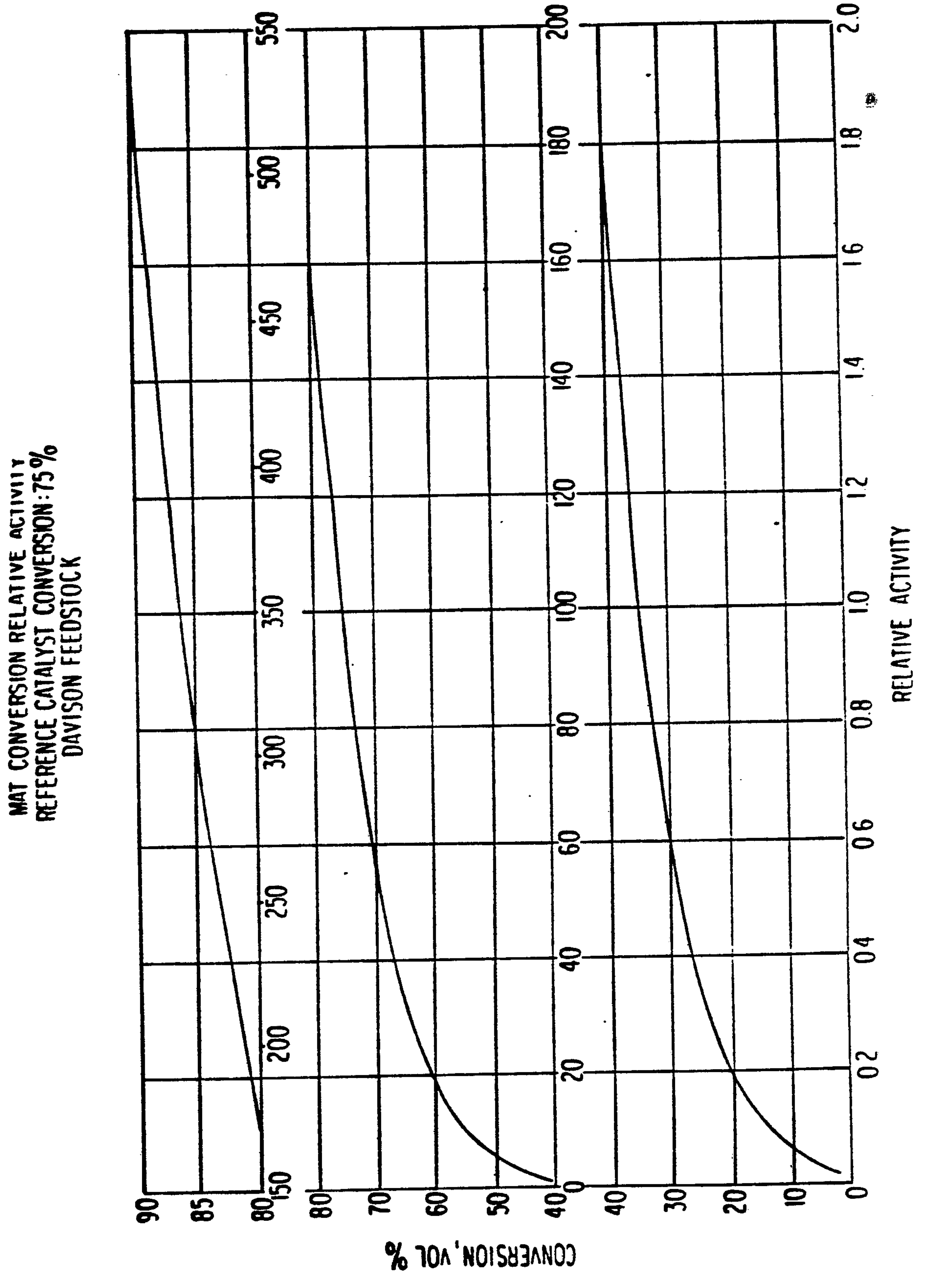

MAT CONVERSION RELATIVE ACTIVITY
REFERENCE CATALYST CONVERSION: 75%
DAVISON FEEDSTOCK

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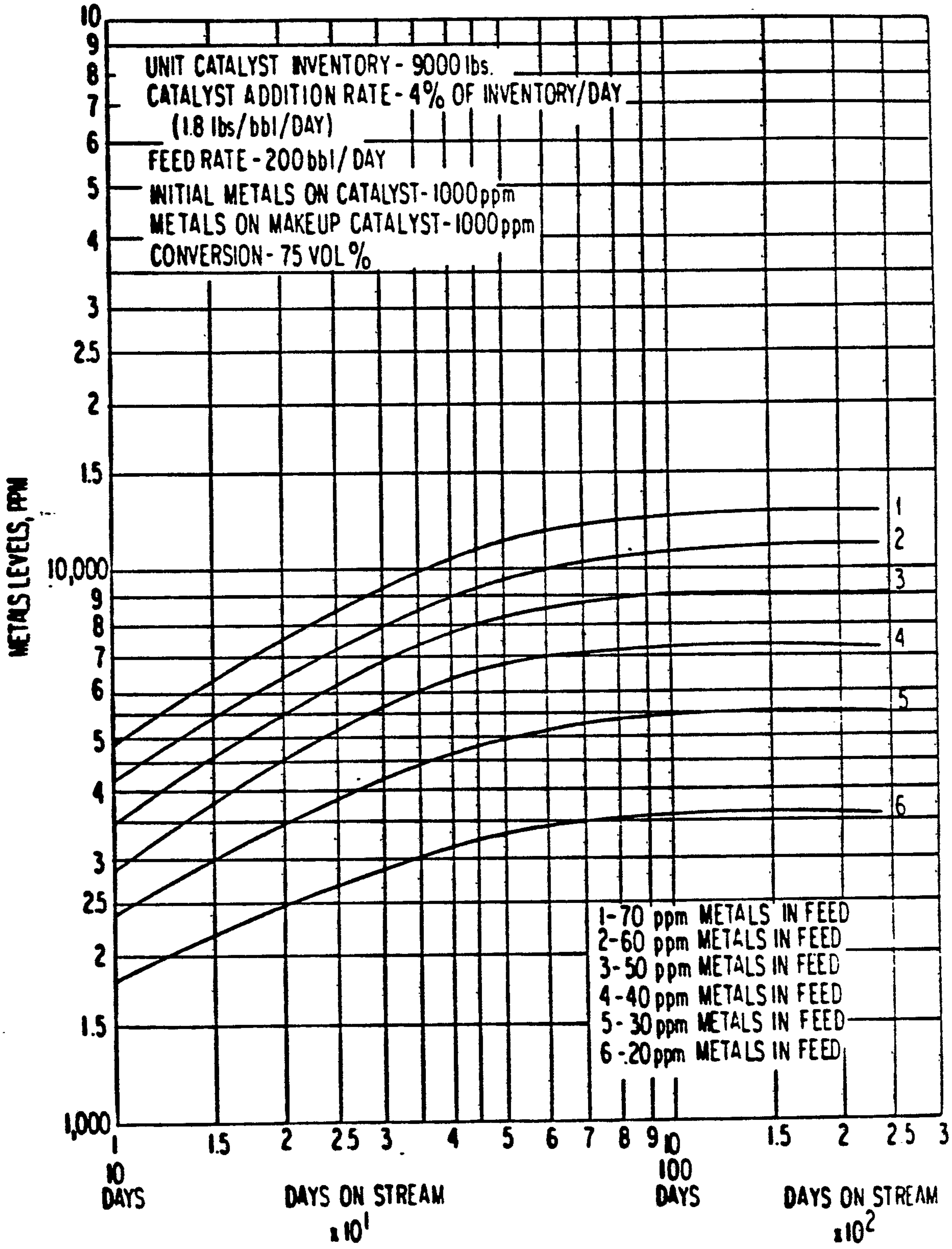
FIG II



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