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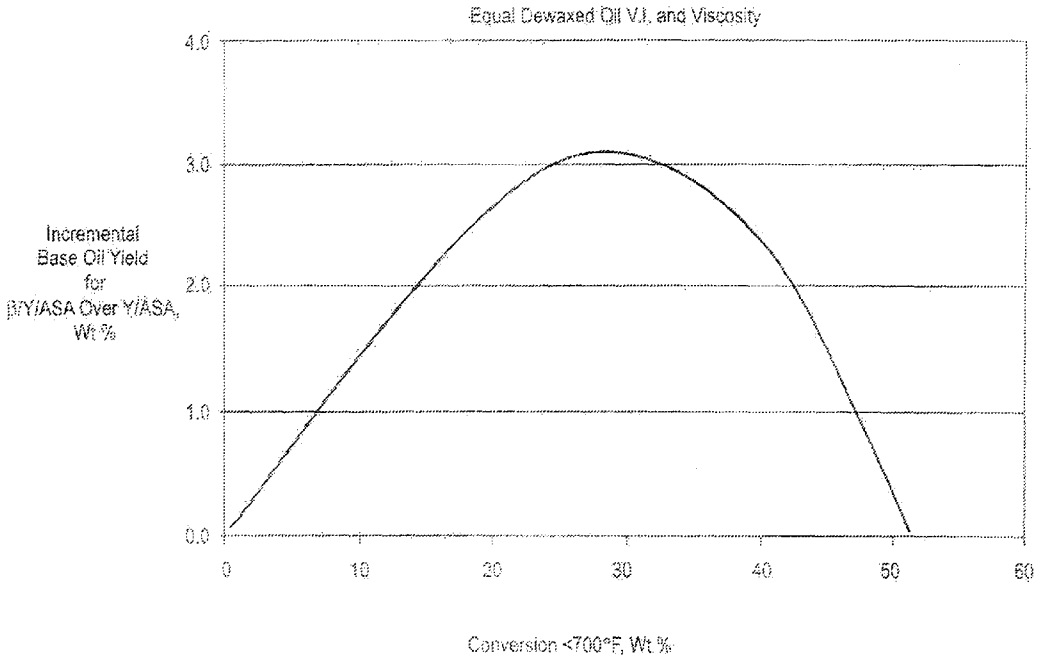
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(54) Title: HYDROPROCESSING CATALYST AND PROCESS OF USE



(57) Abstract: This invention is directed to a catalyst composition effective in hydroprocessing and a process employing this catalyst. The catalyst composition comprises three acidic components acting in synergy to provide enhanced catalytic activity, when compared to any of the components alone or in combinations of two. Two of the components are large pore zeolites, and the third component is selected from the group comprising clays and amorphous silica/alumina.

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HYDROPROCESSING CATALYST AND PROCESS OF USE

This application claims priority from provisional application number US 60/820,907, filed July 31, 2006.

Field of the Invention

This invention is directed to a catalyst effective in hydroprocessing and a process employing this catalyst.

Background of the Invention

The literature of the refining arts contains examples of two acidic components of a hydroprocessing catalyst exhibiting synergy. The two components together are more effective than either component alone in hydroprocessing hydrocarbon feeds.

U.S. Pat. No. 3,535,225, discloses a hydroprocessing catalyst comprising a zeolite such as Y, a faujasite, in combination with an amorphous aluminosilicate.

Combinations of faujasites with clays are also disclosed in GB 1267416, U.S Pat. No. 3716475,and U.S. Pat. No. 3764519.

Summary of the Invention

This application discloses a catalyst composition suitable for hydroprocessing a hydrocarbonaceous feedstock, said catalyst composition comprising three acidic components acting in synergy to provide enhanced catalytic activity when compared to any of the components alone or in combinations of two.

It was discovered that addition of a zeolite having a cage window in the range from about 0.47 nm to about 0.85 nm in diameter (such as zeolite beta), to a combination of a zeolite in the range from about 0.47 nm to about 0.85 nm in diameter, (such as zeolite Y) and amorphous aluminosilicate (ASA) or delaminated clay (such as saponite) significantly enhances the activity, the diesel yield, the heavy diesel cold flow properties, the hydrodenitrification effects, and the base oil yield of the combinations of Y and ASA alone.

Brief Description of the Figures

Figure 1 illustrates the improved base oil yield that occurs when employing the catalyst of this invention.

Figure 2 illustrates the improved dewaxed oil viscosity index that occurs when employing the catalyst of this invention.

Detailed Description of the Invention

Feeds

The feedstocks that may be hydroprocessed using the catalyst of this invention are selected from the group consisting of petroleum distillates, solvent-deasphalted petroleum residua, shale oils, Fischer-Tropsch derived feedstocks and coal tar distillates. The feedstocks contain substantial amounts of materials boiling above 200 ° F, preferably substantial amounts of materials boiling in the range 350 ° to 1100 ° F, and more preferably in the range 400 ° to 1000 ° F. Suitable feedstocks include those heavy distillates normally defined as heavy straight-run gas oils and heavy cracked cycle oils, as well as conventional FCC feed and portions thereof. Cracked stocks may be obtained from thermal or catalytic cracking of various stocks, including those obtained from petroleum, gilsonite, shale and coal tar. The feedstocks may have been subjected to a hydrofining and/or hydrogenation treatment, which may have been accompanied by some hydrocracking, before being

supplied to the hydroprocessing zone organic nitrogen content be less than 100 Parts per million organic nitroen- A preferred range is 0.5 to 1000 parts per million; more preferably, 0.5 to 100 parts per million. When contacting the catalyst of this invention, it is preferable to maintain the organic sulfur content of the feed to a range of from 0 to 3 weight percent, preferably from 0 to 1 weight percent.

Products

The terms "lubes" and "base oils" are used interchangeably in this application and refer to products boiling at or above 700° F. "Fuels" boil in the range from C_5^+ to below 700° F.

Operating Conditions

The hydroprocessing zone containing the catalyst of this invention is preferably operated at hydrocracking conditions including a temperature in the range 400 ° to 950 ° F preferably 500 ° to 850 ° F, a pressure in the range 800 to 3500psig, preferably 1000 to 3000 psig, a liquid hourly space velocity in the range 0.1 to 5.0, preferably 0.5 to 5.0, and more preferably 0.5 to 3.0.

The total hydrogen supply rate (makeup and recycle hydrogen) to the hydroprocessing zone is 200 to 20,000 s.c.f preferably 2000 to 20000 scf of hydrogen per barrel of said feedstock.

Where a separate hydrotreating zone, is located ahead of the hydrocracking zone containing the catalyst of this invention, the operating conditions in the separate hydrotreating zone include a temperature of 400 ° to 900 ° F, preferably 500 ° to 800 ° F, a pressure of 800 to 3500 psig preferably 1000 to 2500 p.s.i.g and a liquid hourly space velocity of 0.1 to 5.0, preferably 0.5 to 3.0. The total hydrogen supply rate (makeup and recycle hydrogen) is 200 to 20,000 s.c.f. of hydrogen per barrel of feedstock, preferably 2000 to 20,000 s.c.f. of hydrogen per barrel of feedstock.

Catalyst composition

The catalyst of this invention comprises three acidic components acting in synergy to provide enhanced catalytic activity. One acidic component is a zeolite having a cage window in the range from about 0.47 nm to about 0.85 nm in diameter. The cage window is the narrowest part of a nanopore system, and the cage is the widest part of the nanopore system. Nanopores are defined as pores smaller than 0.2 nm in diameter. Large pore zeolites such as BEA- (beta), ISV-, BEC-, IWR-, MTW-, SSZ-31-, OFF- (offretite), MAZ- (mazzite), MOR- (mordenite), MOZ-, AFI-, ZSM-48-, and SSY-type zeolites fit this description. These are documented at http://topaz.ethz.ch/IZA-SC/StdAtlas.htm, and in Baerlocher, Meier, and Olson's "Atlas of Zeolite Framework Types", Elsevier, 2001. BEA possesses a Si/Al molar ratio in the range from about 100 to about 300, preferably in the range from about 100 to about 200. The website defines pore diameters of the zeolites mentioned.

The 2nd acidic component is a zeolite having a cage in the range from about 0.9 nm to about 2.0 in diameter. This category includes large pore zeolites such as FAU-, EMT-, ITQ-21-, ERT-, and ITQ-33-type zeolites. FAU, EMT and ERT are further described at the sources indicated above. ITQ-21 is described in an article, "A large-cavity zeolite with wide pore windows, and potential as an oil refining catalyst." Corma, Avelino; Diaz-Cabanas, Maria J.; Martinez-Triguero, Joaquin; Rey, Fermando; Rius, Jordi. UPV-CSIC, Instituto de Tecnologia Quimica, Universidad Politecnica de Valencia, Valencia, Spain. Nature (London, United Kingdom) (2002), 418(6897), 514-517. ITQ-33 is described in the article, "High-throughput synthesis and catalytic properties of a molecular sieve with 18- and 10-member rings." Corma, Avelino; Diaz-Cabanas, Maria J.; Jorda, Jose Luis; Martinez, Cristina; Moliner, Manuel. Instituto de Tecnologia Quimica, UPV-CSIC, Universidad Politecnica de Valencia, Valencia, Spain. Nature (London, United Kingdom) (2006), 443(7113), 842-845. The FAU-type zeolite has a Si/Al molar ratio in the range from about 10 to about 100, preferably in the range from about 10 to

about 80. The catalyst composition of the instant invention comprises active zeolite components ranging from about 1% to about 50% of the catalyst composition.

The 3rd acidic component ranges from about 10% to about 90% of the catalyst composition, and is selected from the group comprising clays and amorphous silica/alumina. If an amorphous silica-alumina component is used, it is preferably selected from the group comprising silica, alumina, titania, zirconia, magnesia and their binary and tertiary compounds. Amorphous silica-alumina component is mesoporous, comprising pores in the range from 2.0 to 50 nm. If a clay is used as the third acidic component, it is preferably selected from a group comprising saponites, vermiculites, biotites, stevensites, hectorite, beidellite, montmorillonites, and nontronites.

In one embodiment of this invention, the first acidic component is beta zeolite, the second acidic component is Y zeolite or USY zeolite and the third acidic component is amorphous silica/alumina.

The catalyst composition of this invention may further comprise a hydrogenation component from the Periodic Table which is selected from a Group VIB metal, a Group VIII metal, or mixtures thereof. Preferably the hydrogenation component is a combination of nickel and tungsten, nickel and molybdenum or cobalt and molybdenum.

Catalyst Preparation

Examples – Catalyst Preparation

Preparation of Co-mul beta/Y/ASA catalyst

A hydrocracking catalyst containing beta/Y/ASA/alumina was prepared per following procedure. 1.4 wt-% beta zeolite (CP811C-300 powder from Süd Chemie), 5.8 wt-% USY (CBV 760 zeolite powder from the PQ corporation), 71.3 wt-% ASA powder (Siral-40 obtained from Sasol), and 21.5 wt-% pseudo-boehmite alumina powder were mixed well. To this mix, nickel nitrate

hexahydrate dissolved in diluted nitric acid were added, so that the total mix contained 0.64 wt-% HNO3, 12.5 wt-% Ni(NO3)2.6H2O, 43 % H2O. To this mix an ammonium metatungstate solution (54.5 wt-% ammonium metatungstentate in water) was added, and enough water to yield an extrudable mix. The paste was extruded in 1/20" asymmetrical quadrulobes, dried at 130 C for one hour and calcined at 510 C for one hour with purging excess dry air. After cooling down to room temperature the catalyst contained 5.1 wt-% NiO and 25.2 wt-% WO3 on a dry basis.

Preparation of Co-mul Y/ASA catalyst

A hydrocracking catalyst containing beta/Y/alumina was prepared as above, but by starting with a powder mix consisting of 5.8 wt.% USY, 72.7 wt.% ASA powder and 21.5 wt.% pseudo-boehmite alumina powder.

Table 1 demonstrates that a catalyst comprising a combination of zeolite beta, zeolite Y and amorphous silica-alumina (ASA) has a higher activity in fuels hydroprocessing applications than a combination of zeolite Y and ASA alone. It results in a larger volume of heavier products.

β/Y/ASA for Fuels Applications: Higher Activity and Heavier Products than Y/ASA

	Y/ASA	β/Y/ASA
Conversion, LV % <700°F	~74	~72
CAT, °F	Base	Base - 27
C_4-, Wt %	3.4	3.3
C_5-180°F, LV %	7.4	6.4
180-250°F, LV %	11.0	9.9
250-550°F, LV %	51.0	48.0
550-700°F, LV %	16.9	20.0
700-EP, LV%	26.4	28.0
N/S, ppm	0.2/12	0.1/8

TABLE 1

Table 2 illustrates improved cold flow improvement properties in fuels hydroprocessing for the catalyst comprising a combination of zeolite beta, zeolite Y and amorphous aluminosilicate(ASA) when compared against a catalyst combination of zeolite Y and ASA alone.

β/Y/ASA for Fuels Applications
Key Product Properties

	Y/ASA	β/Y/ASA
Conversion, LV % <700°F	~74	~72
CAT, °F	Base	Base - 27
Jet Cut / Smoke Point, mm	27	25
Freeze, °C	-62	-63
Heavy Diesel / Pour, °C	-22	-31
Cloud, °C	-10	-8
Cetane Index	63.6	63.0
UCO: N/S, ppm	0.2/10	0.2/<6
Pour, C	34	30

TABLE 2

Table 3 illustrates that a catalyst comprising a combination of zeolite beta, zeolite Y and amorphous aluminosilicate (ASA) has a higher activity in lubes hydroprocessing applications than a combination of zeolite Y and ASA alone.

β/Y/ASA for Lube Applications: Similar
Yields But Higher Activity Than Y/ASA

	Y/ASA	β/Y/ASA
Conversion, LV % <700°F	~40	~40
CAT, °F	Base	Base -- 16
C_4-, Wt %	1.3	1.5
C_5-180 F, LV %	2.1	2.2
180-250 F, LV %	3.6	3.7
250-550 F, LV %	23.4	24.3
550-700 F, LV %	18.4	17.8
700-EP, LV %	59.3	59.6
N/S, ppm	1.2/28	0.1/11

TABLE 3

Table 4 illustrates improved viscosity index and pour point in lubes hydroprocessing for the catalyst comprising a combination of zeolite beta, zeolite Y and amorphous aluminosilicate (ASA) when compared against a catalyst combination of zeolite Y and ASA alone.

β/Y/ASA for Lube Applications
Key Product Properties

	Y/ASA	β/Y/ASA
Conversion, LV % <700°F	~40	~40
CAT, °F	Base	Base -16
Jet Cut / Smoke Point, mm	19	20
Freeze, °C	-62	-61
Heavy Diesel / Pour, °C	-12	-13
Cloud, °C	-9	-5
Cetane Index	47.7	51.7
UCO / N/S, ppm	0.2/29	0.2/12
V.I.	126	127
Viscosity @ 100°C	6.18	6.25
Pour, °C	43	30

TABLE 4

Table 5: Arab Gulf vacuum gas oil (VGO) Feedstock Properties

API gravity 60/60 (1)	20.0
Sulfur (wt-%)	2.76
Nitrogen (wt-%)	0.11
D2887 Simulated Distillation	
IBP	640 °F
10 wt-%	722 °F
30 wt-%	802 °F
50 wt-%	859 °F
70 wt-%	915 °F
90 wt-%	980 °F
End Point	1032 °F

TABLE 5

Conditions: 5000 scf/b, LHSV=0.75, 2300 psi, temperature range 700 ° - 800 ° F. This feedstock was used to generate data of Tables 1-4 and Figures 1 and 2.

Figure 1 illustrates the improved base oil yield that occurs when employing the catalyst of this invention.

Figure 2 illustrates the improved dewaxed oil viscosity index that occurs when employing the catalyst of this invention.

WHAT IS CLAIMED IS:

1) A catalyst composition suitable for hydroprocessing a hydrocarbonaceous feedstock, said catalyst composition comprising three acidic components acting in synergy to provide enhanced catalytic activity when compared to any of the components alone or in combinations of two.

2) The catalyst composition of claim 1, wherein the first acidic component is a zeolite having a cage window in the range from about 0.47 nm to about 0.85 nm in diameter, the 2nd acidic component is a zeolite having a cage in the range from about 0.9 nm to about 2.0 nm in diameter, and the 3rd acidic component is selected from the group comprising clays and amorphous silica/alumina.

3) The catalyst composition of claim 2 wherein the 1st acidic zeolite, and the 2nd acidic zeolite are large pore zeolites.

4) The catalyst composition of claim 3 wherein the 1st acidic zeolite is selected from the group consisting of BEA-, ISV-, BEC-, IWR-, MTW-, SSZ-31-, OFF-, MAZ-, MOR-, MOZ-, AFI-, ZSM-48-, and SSY-type zeolites.

5) The catalyst composition of claim 4 wherein the 1st acidic zeolite is a BEA-type zeolite.

6) The catalyst composition of claim 5 wherein the BEA-type zeolite has a Si/Al ratio in the range from about 100 to about 300, preferably in the range from about 100 to about 200.

7) The catalyst composition of claim 1 wherein the 2nd acidic zeolite is selected from the group comprising FAU-, EMT-, ITQ-21-, ERT-, and ITQ-33-type zeolites.

8) The catalyst composition of claim 7 wherein the 2nd acidic zeolite is a FAU-type zeolite.

9) The catalyst composition of claim 8 wherein the FAU-type zeolite has a Si/Al molar ratio in the range from about 10 to about 100, preferably in the range from about 10 to about 60.

10) The catalyst composition of claim 1 wherein said catalyst composition comprises active zeolite components ranging from about 1% to about 50% of the catalyst composition.

11) The catalyst composition of claim 1 wherein the 3rd acidic component ranges from about 10% to about 90% of the catalyst composition.

12) The catalyst composition of claim 1 wherein the 3rd acidic material comprises at least one amorphous silica-alumina component selected from the group comprising silica, alumina, titania, zirconia, magnesia and their binary and tertiary compounds.

13) The catalyst composition of claim 12 wherein said amorphous silica-alumina component is mesoporous.

14) The catalyst of claim 13, wherein the amorphous silica-alumina component comprises pores in the range from 2.0 to 50 nm.

15) The catalyst composition of claim 1 wherein the 3rd acidic material is a phyllosilicate.

16) The catalyst composition of claim 15 wherein the phyllosilicate is a clay selected from a group comprising saponites, vermiculites, biotites, stevensites, hectorite, beidellite, montmorillonites, and nontronites.

17) The catalyst composition of claim 1 wherein said catalyst composition further comprises a hydrogenation component from the Periodic Table which is selected from a Group VIB metal , a Group VIII metal , or mixtures thereof.

18) The catalyst composition of claim 17 wherein the hydrogenation component is a combination of nickel and tungsten.

19) The catalyst composition of claim 2, wherein the first acidic component is beta zeolite, the second acidic component is Y zeolite or USY zeolite and the third acidic component is amorphous silica/alumina.

20) The process of hydrocracking a hydrocarbonaceous feedstock with a catalyst composition, said catalyst composition comprising three acidic components acting in synergy to provide enhanced catalytic activity when compared to any of the components alone or in combinations of two.

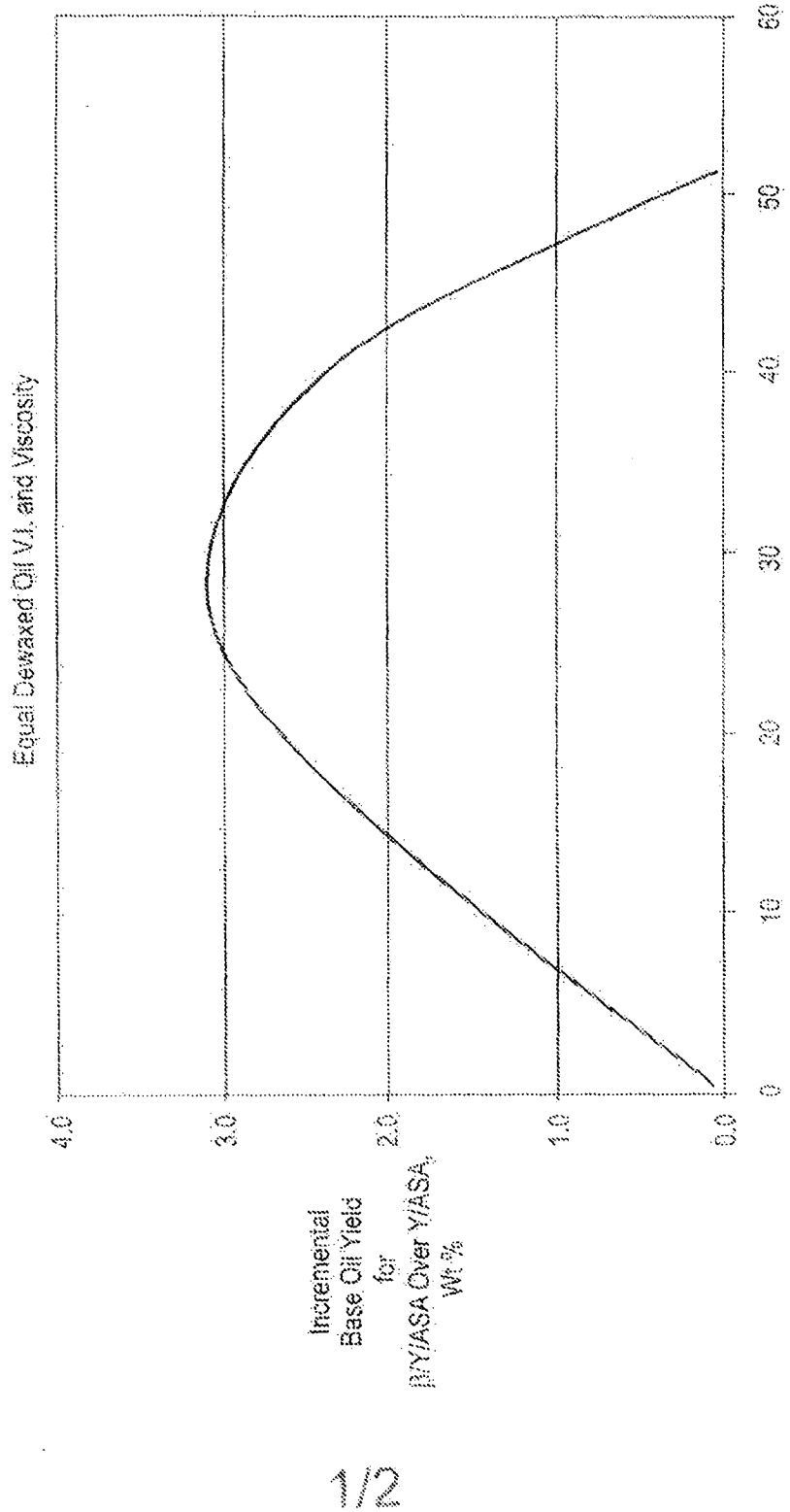

Equal Dewaxed Oil V.I. and Viscosity
Incremental Base Oil Yield for B/Y/ASA Over Y/ASA, Wt %
4.0
3.0
2.0
1.0
0.0
0
10
20
30
40
50
60
Conversion <700°F, Wt %

FIG. 1

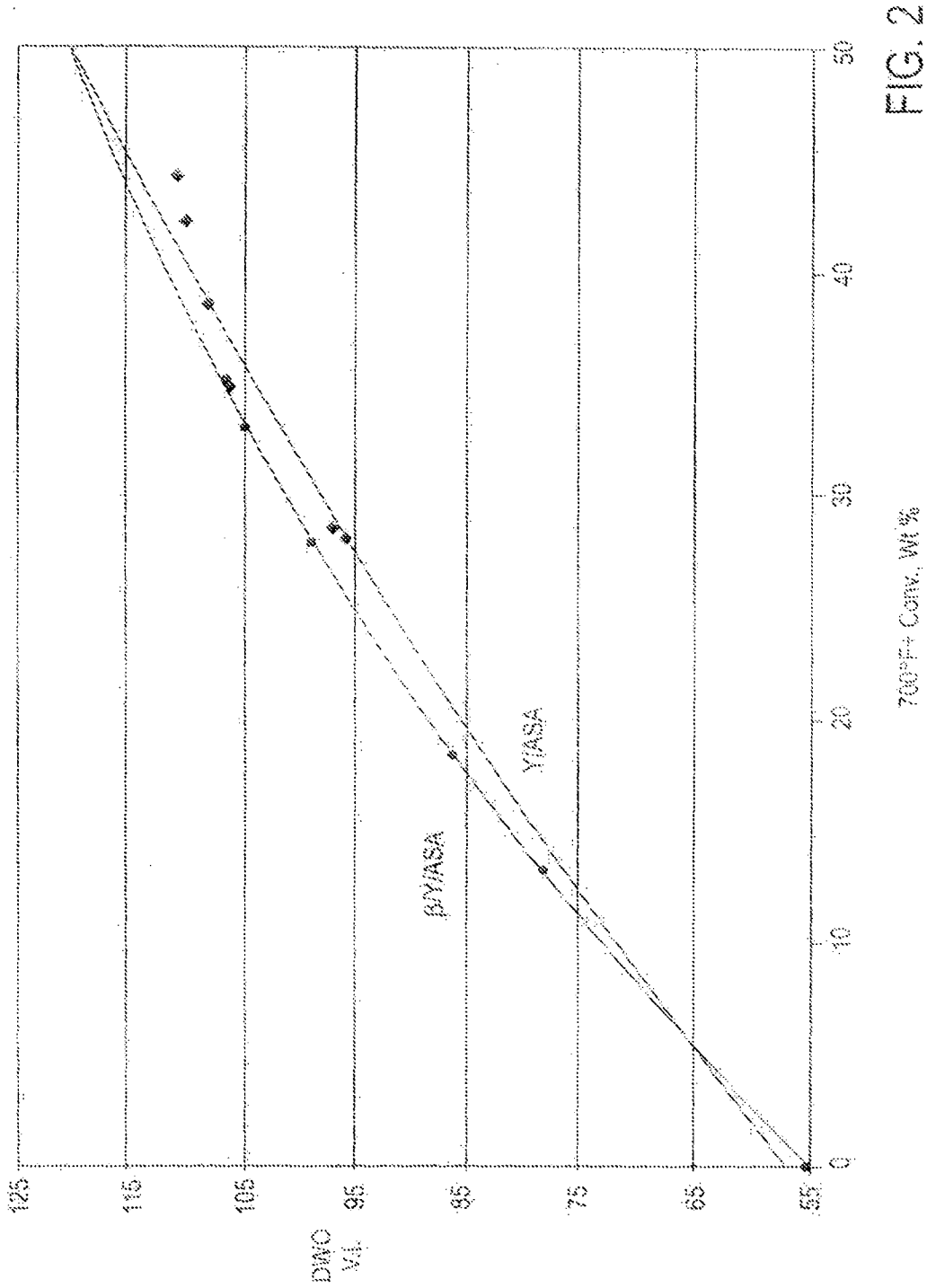

125
115
105
95
85
75
65
55
DWO
Vi
0
10
20
30
40
50
700°F+ Conv, Wt %
Y/ASA
B/Y/ASA

FIG. 2