PLAINTIFF'S EXHIBIT

TEX-43

GULF RESEARCH & DEVELOPMENT COMPANY

PITTSBURGH, PENNSYLVANIA

AMERICAN PETROLEUM INSTITUTE
PROJECT PS-22-GRD(840)
"COMPREHENSIVE ANALYSIS OF PETROLEUM COKE PRODUCTS"

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Report No. 553RL069

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Approved M C Bryson
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API PROJECT NO. PS-22-GRD(840)

"Comprehensive Analysis of Petroleum Coke Products"

Project Summary

Three samples of petroleum coke and one process water were analyzed for polynuclear aromatics (PNA) content and trace metals considered to be toxic. Elemental analysis, X-ray diffraction studies for crystalline components, and scanning electron microscope studies for morphology were also performed on the three coke samples.

All eight metals in the water were determined to be below EPA recommended standards for drinking water. Four PNAs were detected in the water, but at extremely low levels - only one, benzo(a)pyrene, was present at a concentration above one part per billion. Based on these analyses the water should not be considered hazardous to handle, although drinking it would not be recommended.

The three coke samples consisted principally of carbon and hydrogen but contained in addition appreciable quantities of oxygen, sulfur, and nitrogen. Two samples contained high concentrations of mercury (56 and 113 ppm) while the third contained none at all (< 1 ppb). Arsenic was not detected in any of the three, but selenium was found in low (0.7-5.3 ppm) concentrations. All three cokes contained appreciable quantities of vanadium and nickel (60-410 ppm). No crystalline components were found by X-ray diffraction analysis.

Benzene extractibles ranged from 0.15 to 9.94 weight percent. These extracts also contained appreciable quantities of oxygen, sulfur, and nitrogen. All three extracts contained polynuclear aromatics in the parts per million range, two of the samples having fairly high concentrations (11-544 ppm) and one having much lower concentrations (2-10 ppm). This suggests that cautious handling procedures should be employed to prevent exposure to the carcinogenic properties indicated by the analysis.

SEM photomicrographs indicated two of the three coke samples were similar, showing a narrow size distribution of fairly smooth particles. The third sample had a broader size range, with a significant amount of fines, and the particles were irregular, with sharp edges. Particle magnifications ranged from 1000X to 6000X.

"Comprehensive Analysis of Petroleum Coke Products"

Analytical Procedures

Carbon, Gulf Method 1444 -

A Leco combustion procedure which measures carbon dioxide by absorption in a solution of potassium hydroxide.

Mineral Carbon, Gulf Method 1469 -

Leco combustion of the organic carbon remaining after hot hydrochloric acid extraction of the carbonate carbon; calculation by difference.

Oxygen, Shutz-Unterzaucher Procedure -

Pyrolysis of sample in nitrogen at 1100°C to produce carbon monoxide, which is then oxidized to carbon dioxide, absorbed in Ascarite and weighed.

Sulfur, Gulf Method 1462 -

A Leco combustion procedure wherein sulfur is combusted at high temperature (≈2800°F) in an induction furnace to produce sulfur dioxide, which is determined photometrically, based on its bleaching effect on starch-iodine solution.

Nitrogen, Gulf Method 811 -

A mercury-catalyzed Kjeldahl procedure wherein the sample is digested in sulfuric acid to produce ammonium sulfate, which is then released by boiling with strong sodium hydroxide, absorbed in a solution of boric acid, and titrated potentiometrically.

Silicon Dioxide, Gulf Method 1362 -

A gravimetric procedure based on sodium carbonate fusion of the ashed sample residue, followed by dissolution of the melt in hydrochloric acid, dehydration of the silica with perchloric acid, filtration, volatilization of the silica in the precipitate with hydrofluoric acid, and calculation of the precipitate's loss in weight.

Iron Oxide, Gulf Method 1341 -

Iron in a sulfuric acid solution of the ashed sample is reduced to the ferrous state with hydroxylamine hydrochloride, buffered with sodium acetate, and reacted with 1,10-phenanthroline to form an orange-red color, which is measured photometrically at 510 nm and compared to a calibration curve.

Free Silica, Trostel + Wynne Method -

The potassium pyrosulfate fusion melt of a sample is dissolved in hot water which is then neutralized with sodium hydroxide, digested, and filtered through close texture filter paper. The precipitate is washed with water and hydrochloric acid, ignited in a platinum crucible and weighed.

X-ray Diffraction -

Spectra, made on a Phillips Model 12045 X-ray Diffraction Unit, are examined and compared with library spectra to detect and identify crystalline species.

Scanning Electron Microscopy -

Photomicrographs are made at high magnifications using a JEOL Scanning Electron Microscope, Model JSM U-3.

Ash, ASTM Method D 3174 -

Samples, in porcelain capsules, are heated gradually from room temperature to constant weight at 750°C, cooled, and weighed.

Wet Digestion for Metals -

This is a closed system digestion procedure using sulfuric and nitric acids to destroy organic matter in a small amount of sample (1-5 grams). The final nitric acid-free sulfuric acid is diluted with water prior to analysis for metals.

Arsenic, Gulf Method 1410 -

A spectrophotometric procedure wherein arsenic in sulfuric acid is evolved as arsine and reacted with silver diethyldithiocarbamate to produce a red color, which is measured at 540 nm and converted to arsenic concentration by comparison with a calibration curve.

Selenium, APHA Standards Method -

An acid solution of the sample is heated with potassium permanganate to oxidize selenium to selenate, after which it is treated with potassium bromide and sodium peroxide, and distilled as selenium tetrabromide. Excess bromine is removed by precipitation as tribromophenol, and quadrivalent selenium is determined photometrically after reaction with diaminobenzidine and subsequent toluene extraction of the yellow colored salt.

Mercury, EPA Procedure (Gulf Method 1261) -

A cold vapor atomic absorption procedure using aqueous samples oxidized with potassium permanganate, sulfuric, and nitric acids and then digested with potassium persulfate, followed by release of mercury vapors to the AA cell upon addition of stannous chloride.

Vanadium and Nickel, Gulf Method 1175A -

An X-ray fluorescence procedure based on measuring X-ray intensity of the two elements after wet-ashing samples with benzene sulfonic acid (manganese added as an internal standard), igniting to remove carbon, and washing the resultant ash onto glass fibre filter discs with isooctane.

Polynuclear Aromatics, Gulf Procedure -

Column chromatography of benzene extractibles using partially deactivated Woelm alumina and elution with isooctane and benzene.

Second stage column chromatography on the first stage fraction (PNA) of interest using a more highly active adsorbent to yield several subfractions.

Each subfraction is evaporated, concentrated in ethanol and subjected to high-pressure liquid chromatography using Bondapak C_{18}/Corasil packing and water/methanol and tetrahydrofuran/methanol as carrier fluids. Peaks of interest are collected in cyclohexane according to monitoring at 254 nm with a Variscan detector.

HPLC fractions of interest are extracted with water and the cyclohexane portions are concentrated and applied to a cellulose acetate plate developed by a mobile phase consisting of ethanol, toluene and water. The fluorescent band of each desired component is removed, washed with hot methanol, concentrated in n-hexadecane and scanned for absorption in the 240-410 nm range. Identification and quantification are established by reference to prepared absorption spectra.

PETROLEUM COKE ANALYSIS

API Sample No.	3-1-134 Conoco Ponca	4-1-140 Delta	6-1-468 Unocal
Elemental Analysis: Wt %			
Carbon, Gulf 1431	90.17	89.93	84.58
Hydrogen, Gulf 1431	4.26	3.71	2.15
Oxygen, Micro	1.06	1.30	2.56
Sulfur, Gulf 1462	3.45	3.36	6.08
Nitrogen, Gulf 811	1.02	1.10	1.45
Mineral Carbon, Gulf 1469	3.86	22.2	22.2
Free Silica Content: ppm			
X-ray Diffraction	ND[a]	ND	ND
Chemical	26	24	98
Chemical Analysis: Wt %			
SiO_2, Gulf 1362	0.04	0.04	0.04
Fe_2O_3, Gulf 1341	0.06	0.06	0.13
Trace Metals			
Arsenic, Gulf 1410: ppb	< 1	< 1	< 1
Selenium: ppm	0.7	4.5	5.3
Mercury, Gulf 1261: ppm	56	< 1	113
Vanadium, Gulf 1175A: ppm	120	145	410
Nickel, Gulf 1175A: ppm	60	95	160
Ash/ ASTM D 3174: Wt %	0.24	0.21	0.81

a. No crystalline components observed.

ANALYSIS OF BENZENE EXTRACTIBLES

API Sample No.	3-1-134	4-1-140	6-1-468
Elemental Analysis; Wt %			
Carbon, Gulf 1431	86.31	88.16	82.85
Hydrogen, Gulf 1431	8.05	6.04	11.94
Oxygen, Micro	0.92	0.89	3.75
Sulfur, Gulf 1535	3.62	4.15	1.97
Nitrogen, Gulf 1258	0.66	0.71	0.14
Benzene Extractibles: Wt %	9.94	~~0.41~~ 1.79 nks	0.15
Polynuclear Aromatics: ppm (Gulf Methodology)			
Benzo(a)pyrene	10	440	50
Benzo(e)pyrene	4	110	197
Benzo(g,h,i)perylene	9	439	276
Benzo(a)anthracene	4	544	38
Dibenzo(a,h)anthracene	4	ND*	35
Chrysene	2	126	138
Pyrene	8	ND	314
Benzo(b)fluoranthene	ND	ND	176
Phenanthrene	ND	ND	280
Methyl Benzo(a)pyrene	ND	ND	32
Fluorene	ND	11	ND
Benzo(g,h,i)fluoranthene	ND	ND	ND
Benzofluorenes	ND	ND	ND
Perylene	ND	ND	ND
Coronene	ND	ND	ND

* ND - Not detected. Estimated lower detectability limit is 1 ppm, based on sample size used.

METALS IN WATER

(Petroleum Coke Process)

API Sample No.	7-1-100	EPA Limits
Metals Analysis: ppb		(Maximum)
(EPA Protocol for Drinking Water)		
Arsenic	< 5	50
Barium	600	1,000
Cadmium	< 5	10
Chromium	< 10	50
Lead	< 10	50
Mercury	< 1	2
Selenium	< 10	10
Silver	< 5	50

PETROLEUM COKE ANALYSIS

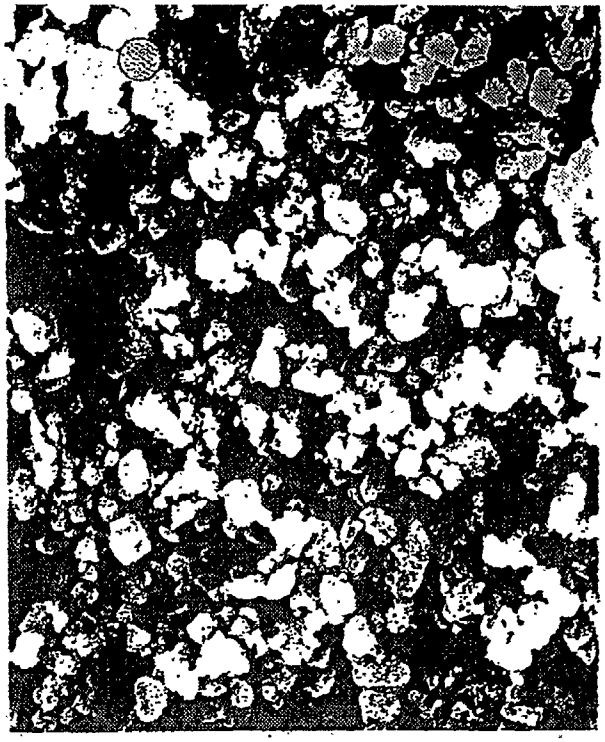
Scanning Electron Microscopy

Samples API 3-1-134 and API 4-1-140 are similar, showing a narrow size distribution of fairly smooth particles.

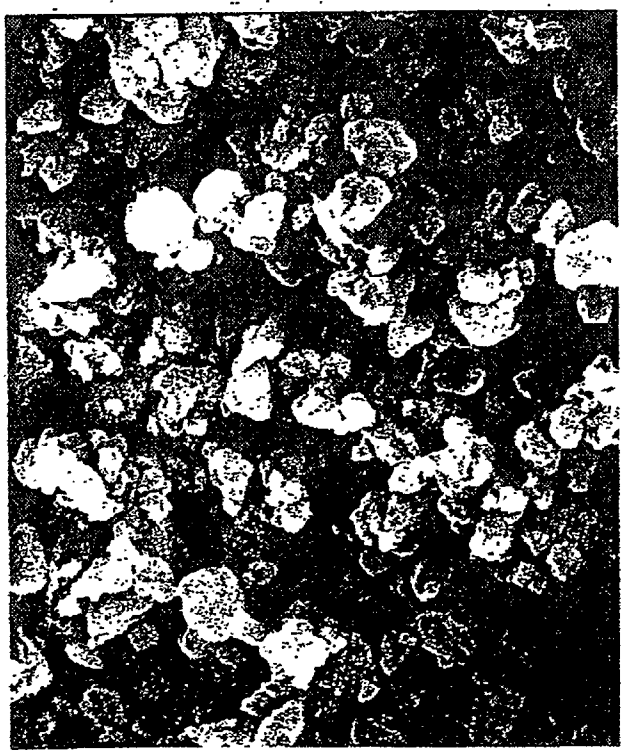
Sample API 6-1-468 is different. Particles are irregular and have sharp edges. The size range is broader and a significant amount of fines (< 1 micron) is present.

Copies of SEM photomicrographs are attached.

API 3-1-134 0 1K



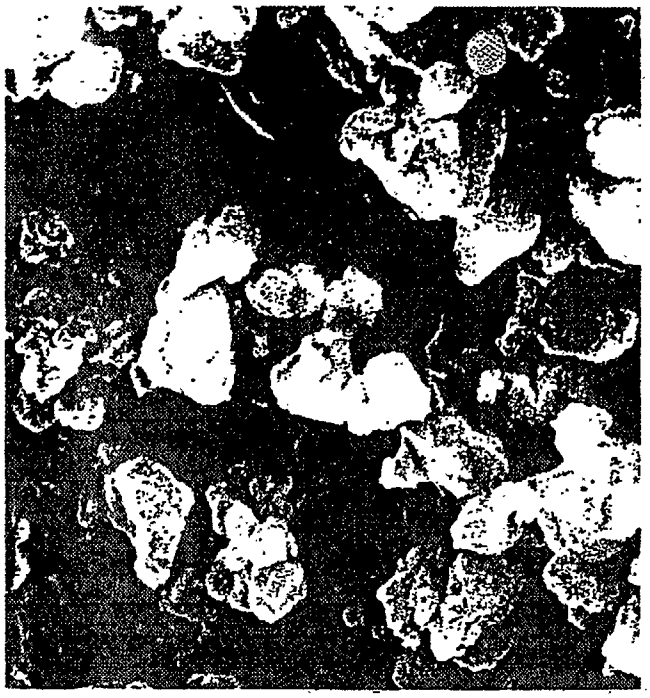
API 3-1-134 0 2K



API 3-1-134 0 3K

API 3-1-134 0 6K

WA-TEX 009098



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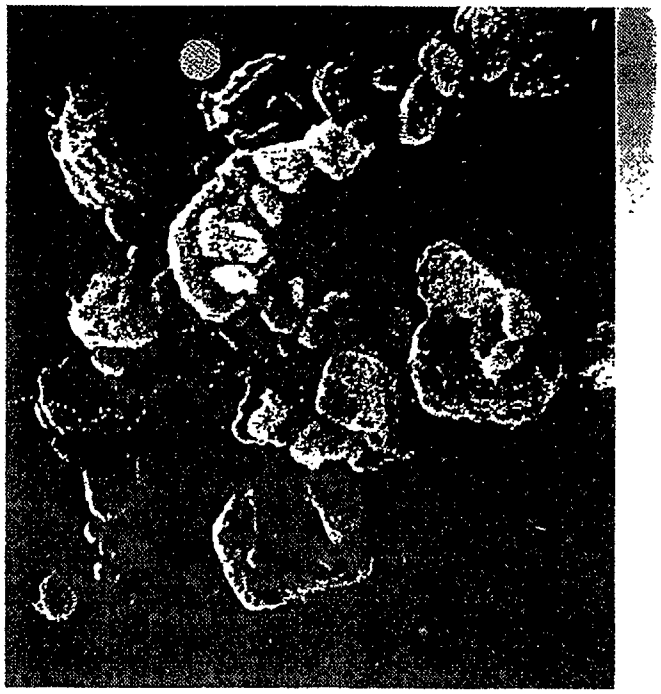

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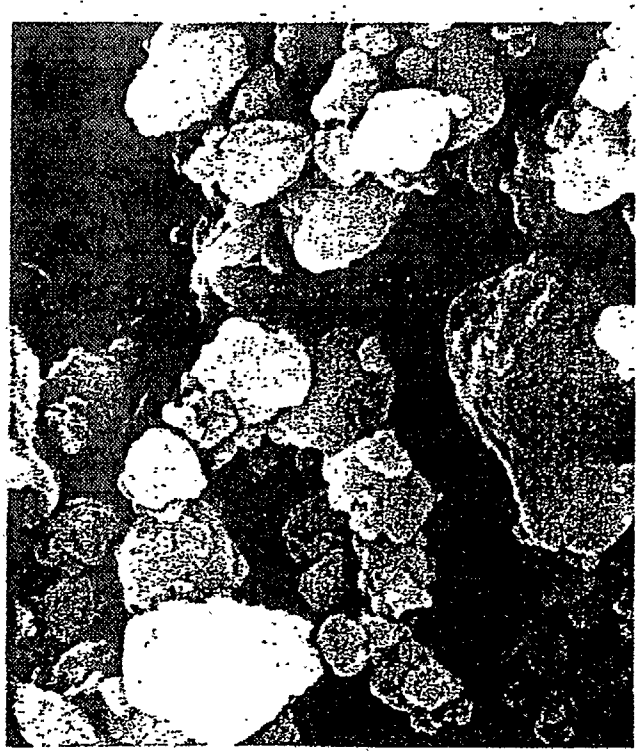

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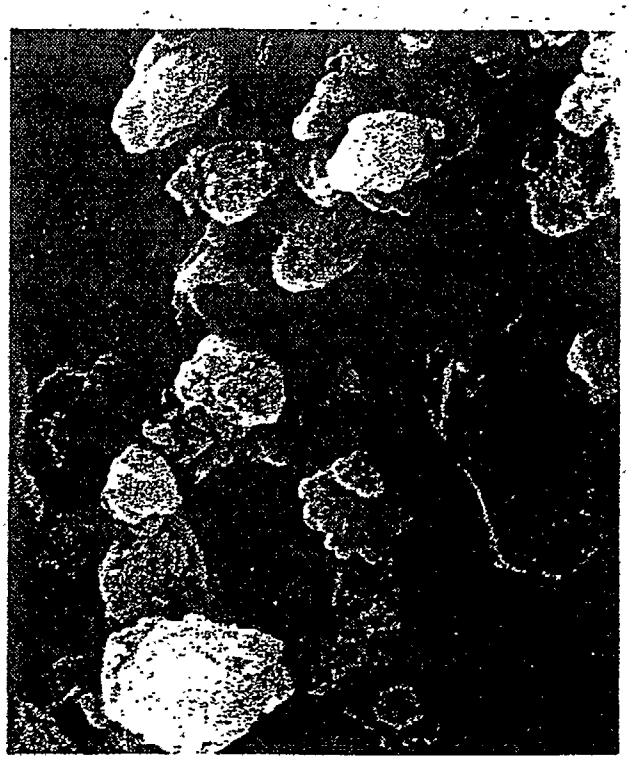

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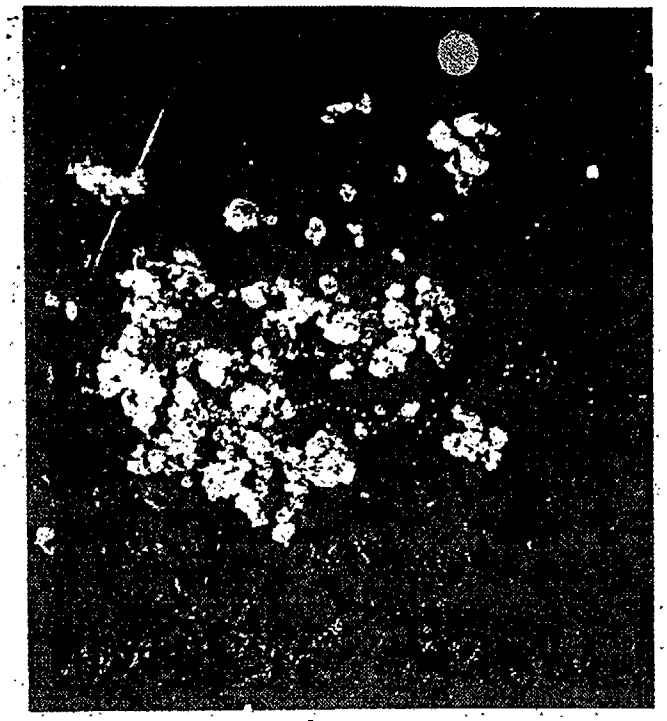

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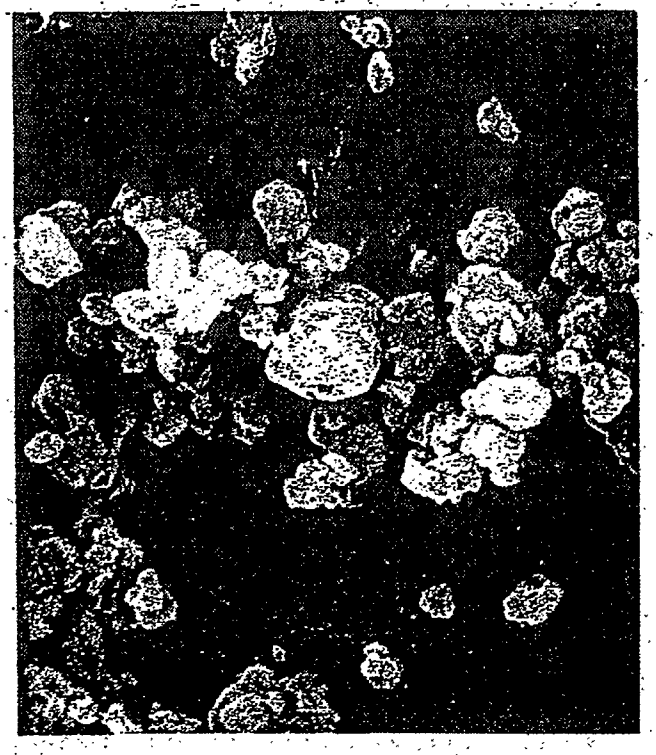

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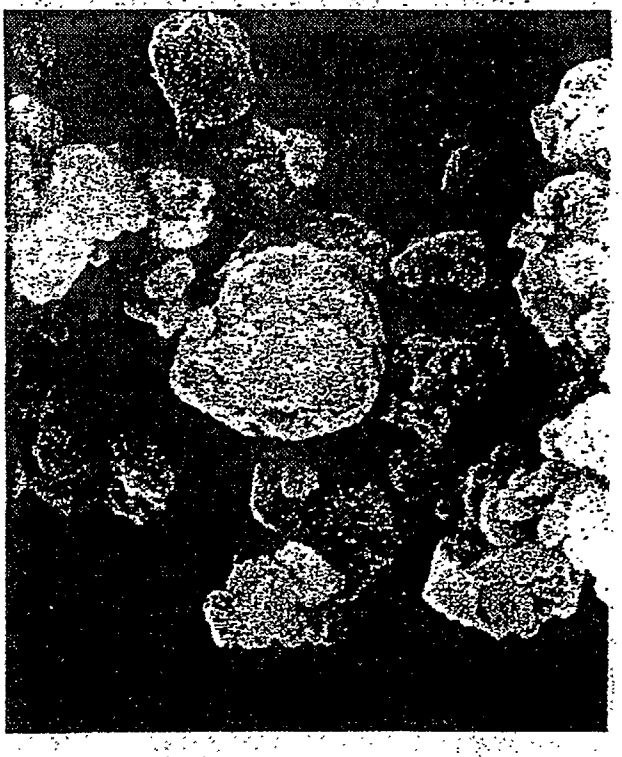

API 3-1-134 (U) 6K

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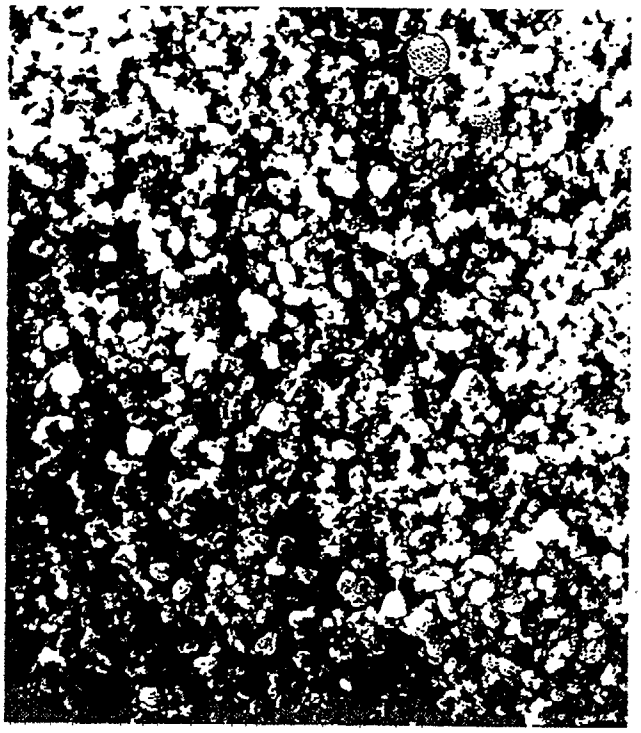

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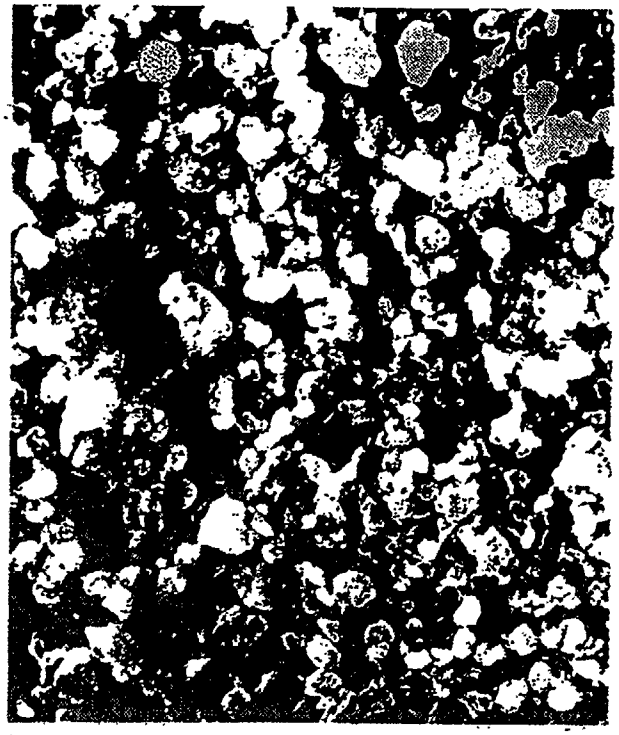


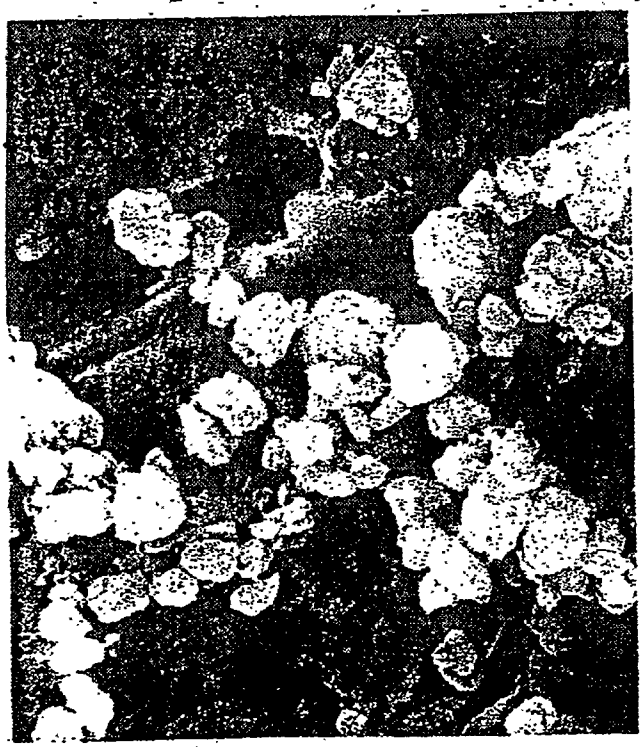
API 3-1-134 ⓧ 2K

API 3-1-134 ⓧ 6K

WA-TEX009101

API 3-1-134 T 1K

API 3-1-134 T 2K



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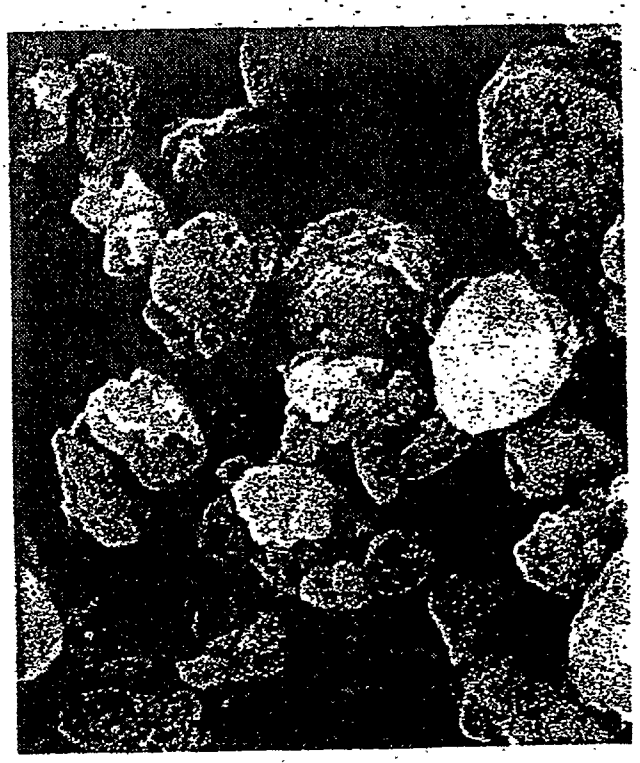
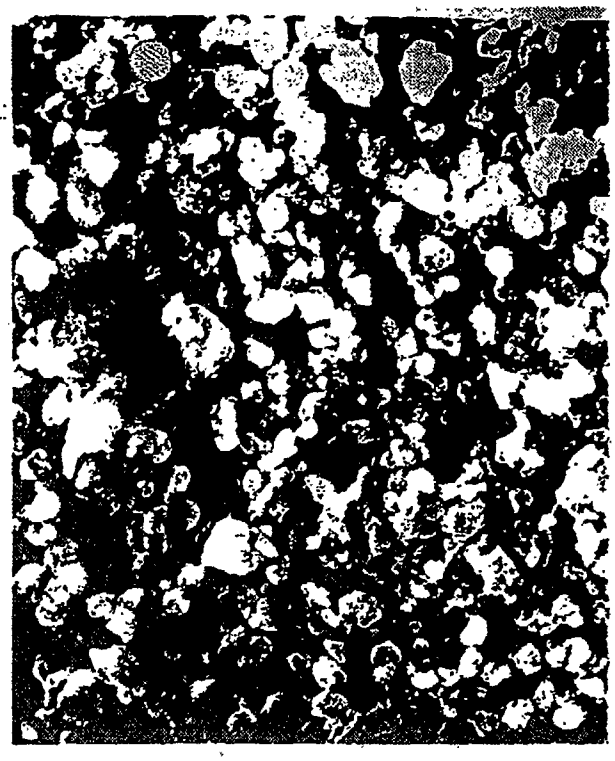


API 3-1-134 T 6K

WA-TEX 009102

API 3-1-134 (X) 1K



API 3-1-134 (X) 2K

API 3-1-134 (X) 6K

WA-TEX 009103

API 6-1-468 ① 1K

API 6-1-468 ① 2K

API 6-1-468 ① 3K

API 6-1-468 ① 6K

WA-TEX 009104

API 6-1-468 ③ 1k

API 6-1-468 ③ 2k

API 6-1-468 3 3k

API 6-1-468 ③ 6k

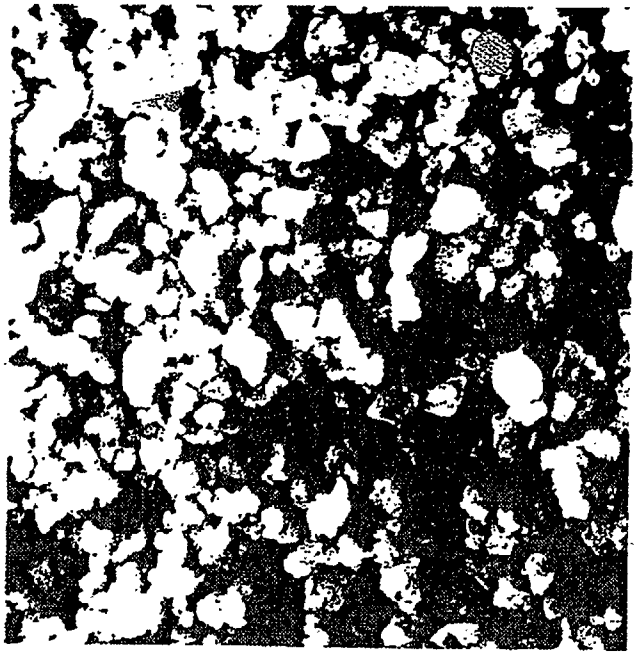
WA-TEX 009105

API 6-1-468 (2) 2k

API 6-1-468 (2) 3k

API 6-1-468 (2) 6K

WA-TEX 009106



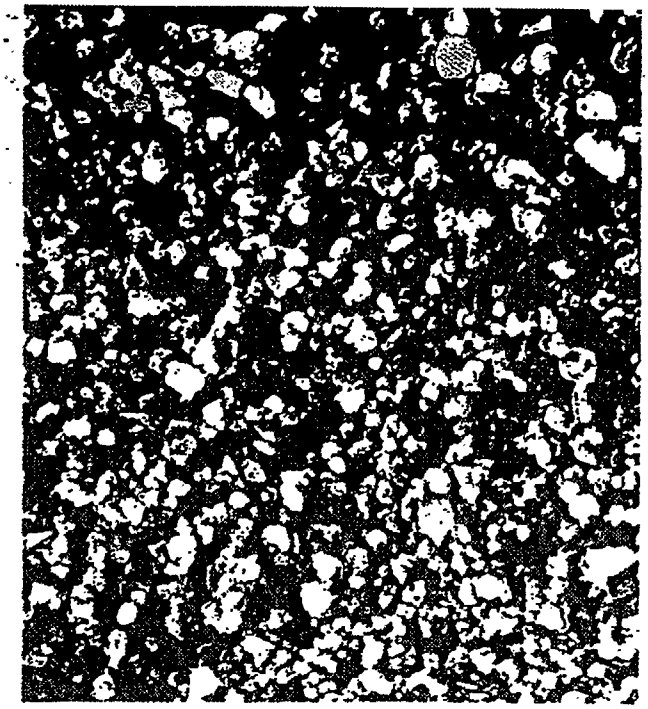
API 4-1-140 ① 2K

API 4-1-140 ① 3K

API 4-1-140 ① 6K

API 4-1-140 ① 6K

WA-TEX009107



API 4-1-140 ② 1K

API 4-1-140 ② 2K

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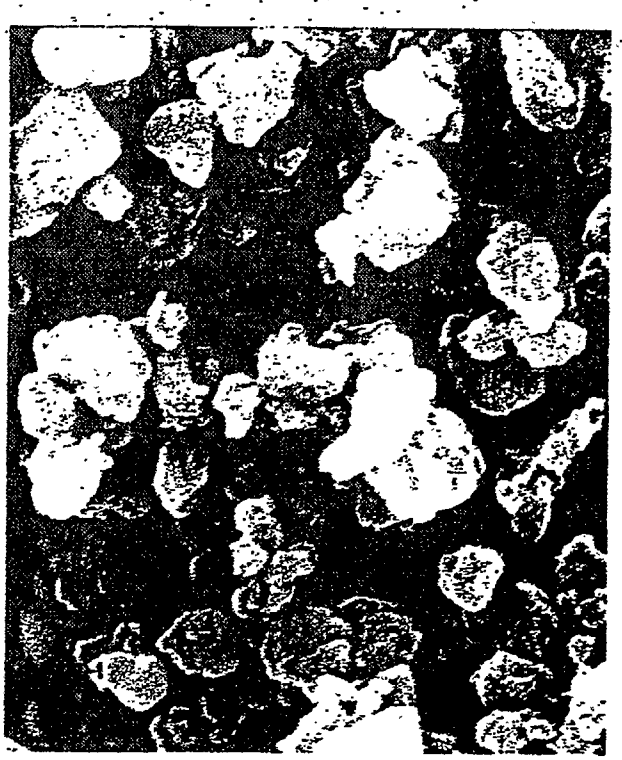

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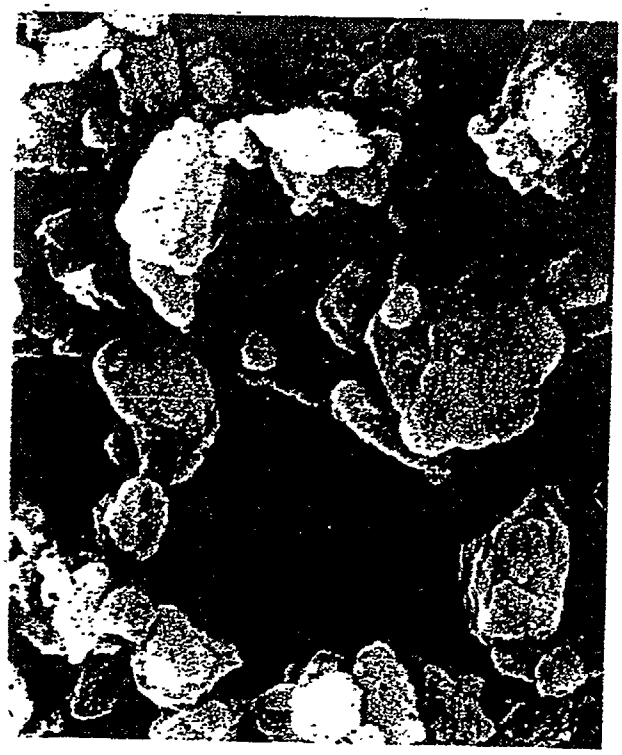

API 4-1-140 ④ 6K

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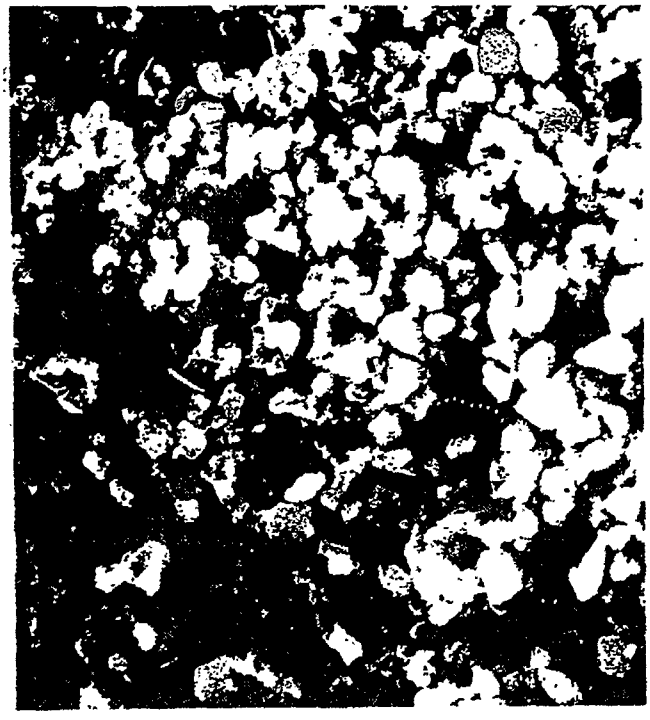

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API 4-1-140 ⑥ 6K

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