High Pressure Experimental Department,
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Abstract on
OPERATING PROCEDURES FOR THE CHARACTERIZATION AND
DECOMPOSITION OF ASPHALTS

by Suida and Mota, Petroleum vol. 35, No. 30 (1939), with information on the methods used in Lunna.

Our knowledge on the nature and composition of asphalts is limited. Chemically identifiable constituents acid compounds, saponifiable compounds and other oxygen compounds; S compounds present with the hydrocarbons with no information available on their composition. For those reasons, characterization mostly made on the strength of physical data (sp. gr., viscosity). Fractional solution and determination of the size of fractions. These data do not give complete information to judge the practical usefulness of asphalts. They merely characterize a certain condition of the asphalts.

A decomposition is required to draw conclusion on changes in the asphalts, as well as its stability.

A large number of investigators have made many tests and investigations in this field. Richardson was one of the first amongst them, who decomposed the asphalts into:

Petrolenes	volatilizable	
Malthenes	soluble in gasoline	
asphaltenes	"	in CCl_4
Carbenes	"	in CS_2
Asm-bitumens		

Others selected other solvents, and a new idea was finally applied, of using adsorption media. Marcusson and Picard used activated charcoal and bleaching earth. Suida and Kamptner used bleaching earth, and Poll, finally, used various solvents with bleaching earth. He has made a distinction between petroleum constituents, petroleum resins, asphalt resins and hard asphalts (carbenes and carbonides; carbenes soluble in CS_2, insoluble in CCl_4; Carbonides insoluble in all the solvents). Poll's method was widely acclaimed and has been accepted in literature as a good and exact method for the characterization of asphalts. We may illustrate how frequently and widely opinions differ by saying that Kamptner opposed adsorptive media for a while, and returned to them later with Mass used activated charcoal of certain activity.

Mallenstein took a stand definitely opposing the opinion that the difficultly soluble constituents of the asphalts were hydrocarbons in mutual solution. He considered asphalts as colloidal systems of dispersed C in an oil as the dispersion medium. Results obtained by decomposition hardly can furnish a basis for the separation of asphalts into chemical groups. Asphalts may well be distinguished by their origin. The older an asphalt (geologically) the larger the proportion of the difficultly soluble and most difficultly soluble constituents. Changes brought about by oxidation are manifested by increased proportion of hard asphalts.

while natural or straight run asphalts not changed by oxidation contain higher proportion of soft asphalts, which permits a ready differentiation of blown asphalts from distillation asphalts. All the more detailed investigations show a clear line of demarkation between the oil constituents of the asphalts and the difficultly soluble asphalts, forming a continuous series up to free C.

The molecular weights increase steadily from the oil constituents to free carbon. The systems change gradually from true solutions, through colloidal dispersions, to the coarse dispersions.

All results obtained by the methods of decomposition by solution and flocculation depend on the proportion of amount of solvent to the amount of extract, and in case of flocculation on the proportion of the flocculant to the amount flocculated. When solution and adsorption methods are used jointly, we get not only a greater probability of obtaining reproducible results, but also strictly comparable values for different asphalts. Adsorption equilibria are very sensitive to temperature changes, but independent within wide limits from dilution.

Every possibility of polymerization must naturally be avoided by keeping O_2 absent. There is not a single exact literature reference, according to which either bleaching earth or activated charcoal act as polymerizing agents when no oxygen is present, and the temperatures are low.

All the methods so far developed, including that of Foll, consume much time, and are not sufficiently reproducible. Suida and Metz have developed a method which reduces to a great extent the errors of manipulation by being automatic, simplifies the operating technique and saves much time.

Suida-Metz method.

10 g. freshly dried bleaching earth is weighed into an extraction thimble (45 x 123 mm). The thimble is placed in the apparatus, and 200 mls $CHCl_3$ added. The mixer head is attached, and by starting the mixer, the earth is uniformely distributed through the thimble. The temperature is maintained at 20°C.

1 g. of the substance to be studied is now weighed into a small glass flask, dissolved in 30 mls $CHCl_3$, the solution carefully transferred to a dropping funnel, and dripped into the extractor maintained at 20° using 30 minutes for the operation. In this way the adsorption upon the bleaching earth is perfect. The mixer flask and the dropping funnel are now rinsed with $CHCl_3$, the slow addition to the extractor continued until the solution is syphoned off into the flask. N_2 is led into the flask through a capillary to exclude oxygen as well as to equalize boiling. The flask is set into a water bath. The extraction is continued at 20° until the $CHCl_3$ running out of the extraction thimble is colorless. The contents of the flask are then rinsed into a dish, $CHCl_3$ evaporated, and a mixture of petroleum oils and resins is left behind.

A fresh flask is now substituted, N_2 or CO_2 led in through a capillary tube for about 1 hour, until $CHCl_3$ has been driven off. 300 mls. pyridin are then slowly added through the dropping funnel, and the extraction carried out at 20° with pyridine. The oil bath temperature is now maintained at 180 - 280° (?) The main portion of pyridine is then distilled off at the end of two hours, the residue in the flask precipitated with dilute HCl, pyridine and water well washed out, and the precipitated asphalt dissolved in benzol or CS_2.

Asphalt resins remain after evaporating the solvent. A tube in the cooler is now removed, the flask again filled with 300 mls pyridine and the extraction repeated at 50°. The extract is worked up as before; the remaining residue consists of hard asphalts.

Changes in equipment to meet the requirements in Leuna:

1) removal of solids with pyridine and CS_2 must be done to obtain the total asphalts. If solids are not removed, poor or non-reproducible results are obtained because of the formation of pockets in the Fuller's earth.

2) Oil and oil resin are separated into their constituents by taking advantage of the fact, the oil resins are insoluble in benzol solution if precipitated upon Fuller's earth.

/signed/ Lemme

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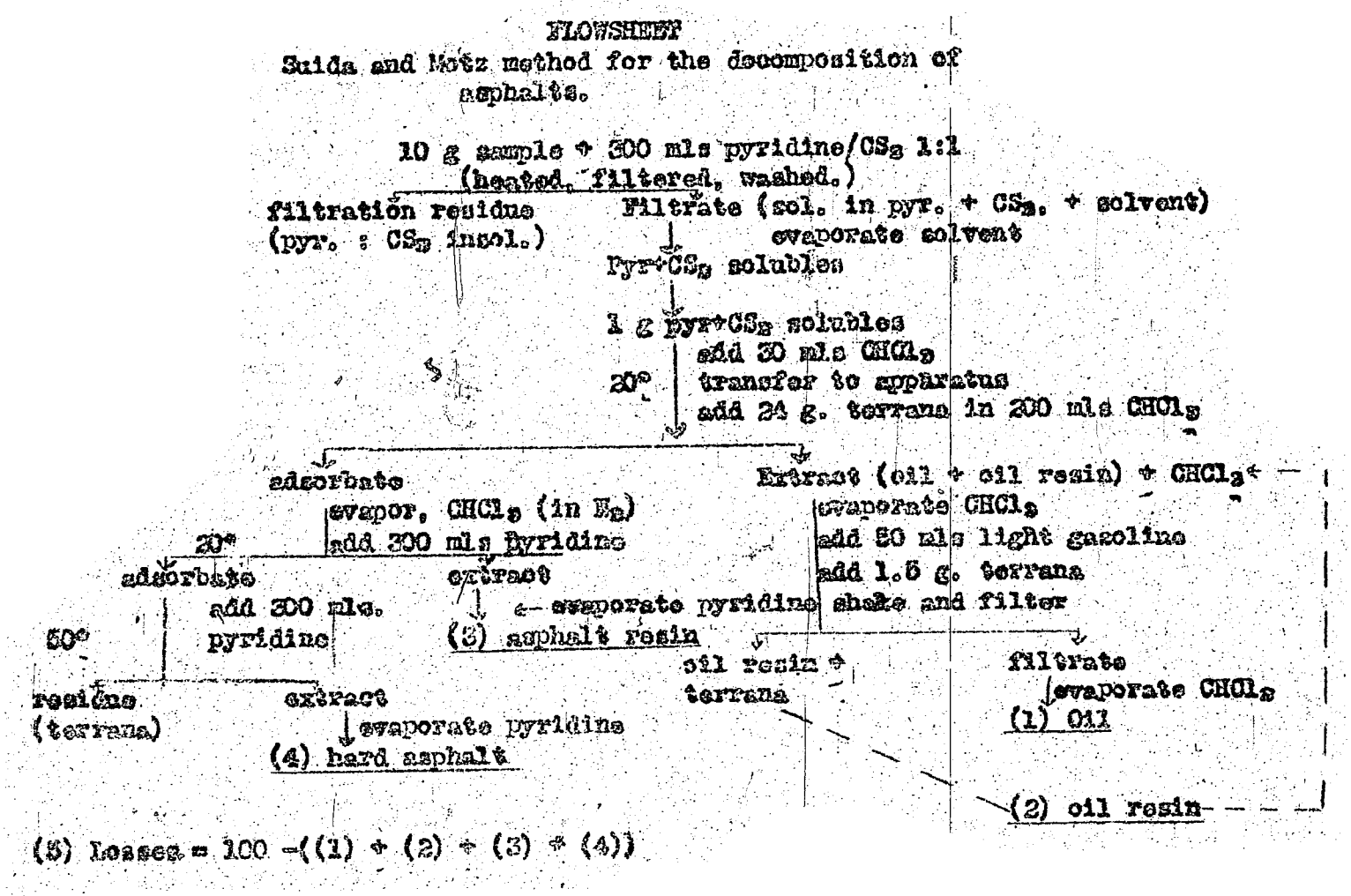
FLOWSHEET

Suida and Motz method for the decomposition of asphalts.



10 g sample + 300 mls pyridine/CS_2 1:1
(heated, filtered, washed.)

filtration residue
(pyr. : CS_2 insol.)

Filtrate (sol. in pyr. + CS_2. + solvent)
evaporate solvent

Pyr+CS_2 solubles

1 g pyr+CS_2 solubles
add 30 mls $CHCl_3$
20° transfer to apparatus
add 24 g. terrana in 200 mls $CHCl_3$

adsorbate
evapor. $CHCl_3$ (in E_2)
add 300 mls pyridine

20°
adsorbate
add 300 mls. pyridine

50°
residue
(terrana)

extract
evaporate pyridine
(4) hard asphalt

extract
← evaporate pyridine
(3) asphalt resin

Extract (oil + oil resin) + $CHCl_3$
evaporate $CHCl_3$
add 50 mls light gasoline
add 1.5 g. terrana
shake and filter

oil resin +
terrana

filtrate
evaporate $CHCl_3$
(1) Oil

(2) oil resin

(5) Losses = 100 -((1) + (2) + (3) + (4))

DECOMPOSITION OF ASPHALTS BY THE SUIDA AND MOTZ (Leuna)

and Scholven methods

HOLD	Leuna (Stall 804) gasoline/middle oil	" Polits	Scholven	Gelsenberg
Insolubles in:				
Pyridine + CS_2	12.0	14.0	18.6	19.5
Pyridine	17.2	13.7	21.2	18.9
$CHCl_3$	19.2	16.4	28.6	20.8
Benzol	20.4	18.9	30.0	21.5
CCl_4	25.5	23.8	38.0	23.3
S-asphalt in:				
Benzol	16.4	18.3	29.5	14.0
Pyridine	17.5	21.1	30.3	14.7
Decomposition (Suida and Motz, Leuna)				
Oil	42.2	40.7	46.9	50.7
Oil resin	28.5	29.1	30.7	29.1
Asphalt resin	14.5	5.8	6.4	9.5
Hard asphalt	16.1	22.0	15.2	9.6
Losses	0.7	2.4	1.1	1.1
Decomposition, Scholven				
A asphalt	2.0	2.7	7.4	1.9
B asphalt	1.2	2.5	1.4	0.7
C asphalt	5.1	4.9	9.0	1.8
A + B + C asphalt	8.3	10.1	19.8	4.4
Oil resin	4.7	3.2	16.7	10.1
Oil	69.8	71.0	45.3	66.6

A asphalt = $CHCL_3$ insol. -Pyrid. insol. B asphalt = bengol insol. - $CHCl_3$ insol.
C asphalt = insol. CCl_4 - insol. benzol Oil resin = CCl_4 sol. - neutr. oil.

- 5 -

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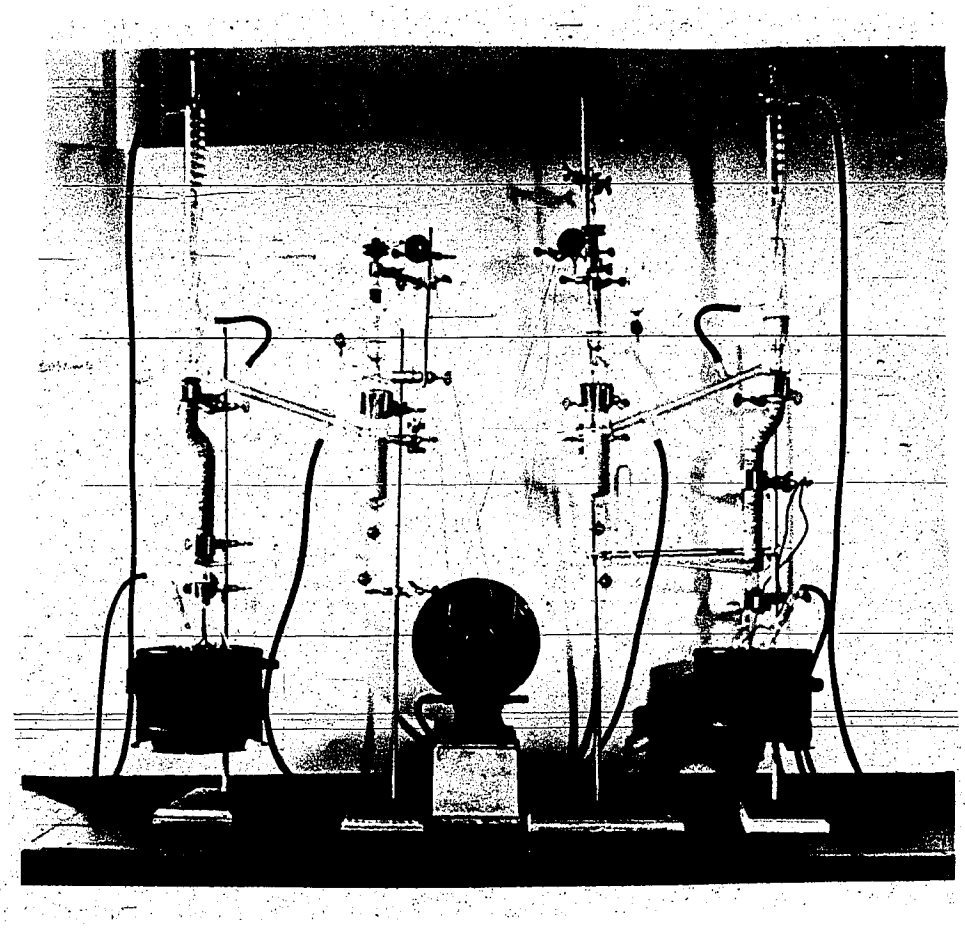
T-398

T-398

1090



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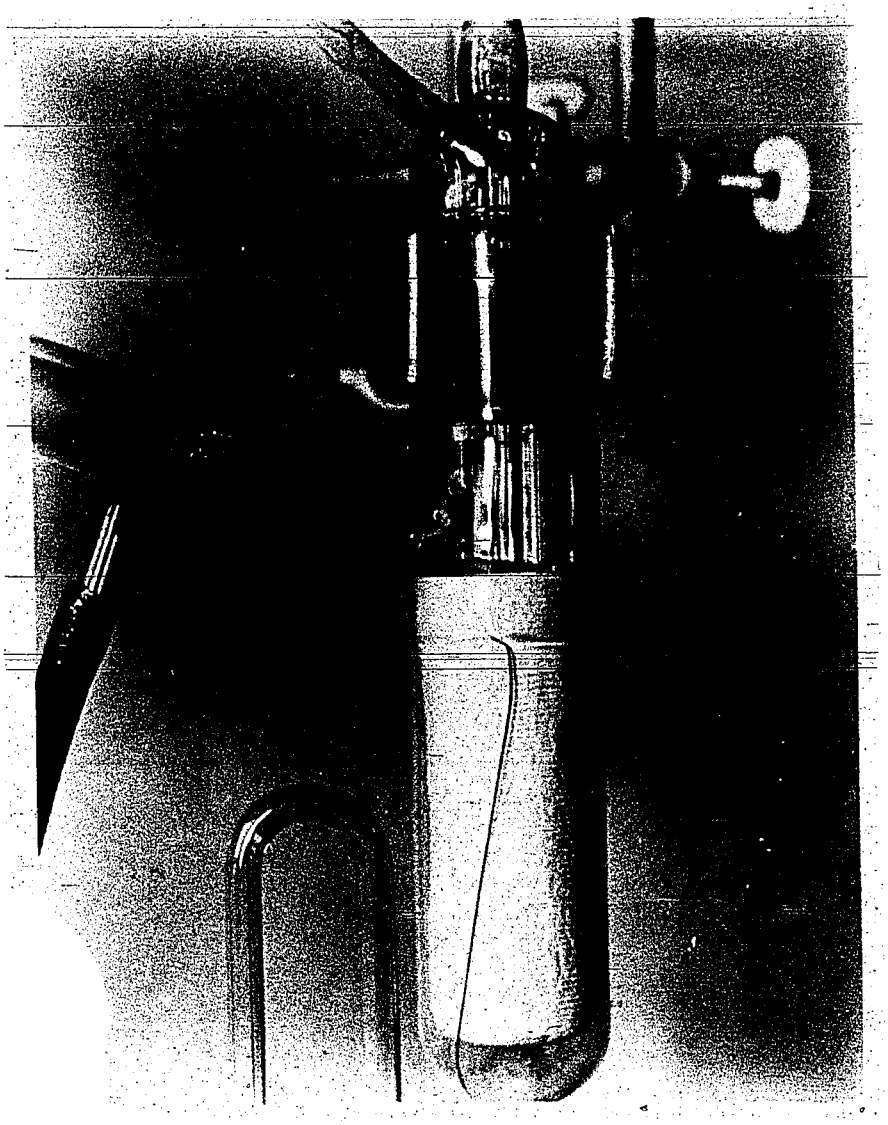
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