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## The Caking of Bituminous Coal.

### Chemical Changes of the Coal Constituents Occurring in the Temperature Range below the Plastic State

By

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In the previous paper<sup>1)</sup>, some considerations relating to the caking of bituminous coal were offered based upon the results obtained by experiments on benzene-extraction and the determination of the swelling power as it varied with some changes in the condition of heating and of the fluidity by a Gieseler plastometer. A hypothesis relating to the changes in fluidity according to the rank of coal, was also drawn from those results.

In the present paper, considerations respecting why the plastic state does not develop in the low rank bituminous coal, will be presented. The considerations are based on the chemical changes in the coal constituents due to thermal action within the temperature range up to the plastic state. It will be, therefore, described from a chemical view-point, but it differs somewhat from the classical theories concerning the caking components in the coal. It must, however, be recognized as an important factor concerned with the caking that the physical properties of coal vary with its quality. The physical theories described by Berkowitz<sup>2)</sup> and others<sup>3)</sup> must be of very much interest.

The principal consideration presented in this paper, however, may be recognized as an essential factor related to the caking of the coal which is of high volatile-matter content and of high fluidity.

In our country, most of the caking coal being of high volatile-matter content, the coal for blast-furnace use is mostly imported. Investigations relating to the caking, therefore, have necessarily been concentrated upon the fingery fissures developed in the coke from the highly volatile caking coal.

There are two important points in seeking a solution of the problem; the one is to reveal the differences in the coal constituents between the low rank bituminous coal and the caking coal having high volatile-matter, as well as in their behaviours in carbonization. The other is

to reveal those differences between the highly volatile caking coal and medium or low volatile-matter one which is the good coking coal.

In this paper, the investigation respecting the first procedure is described. In a later paper the problems relating to the second approach will be discussed.

### Influences of the rate of heating upon the plastic properties.

It is well known that the plastic properties are affected by the rate of heating no matter by what method they are measured.

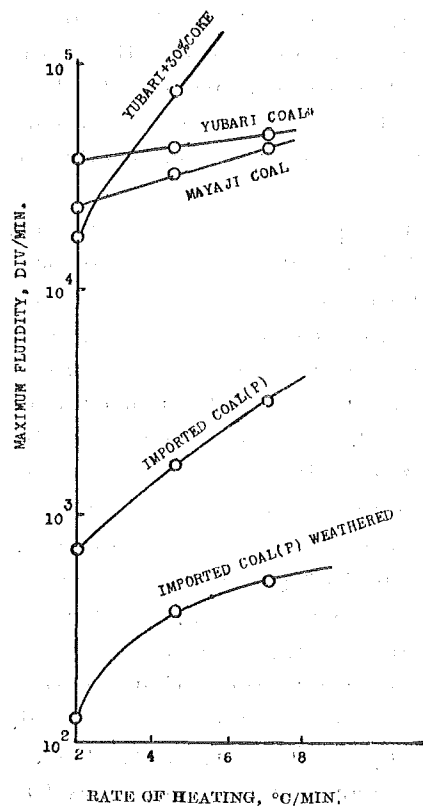


Fig. 1. Changing states of the maximum fluidity due to a variation of the rate of heating.

\* These values were measured at when the torque on the stirring-shaft was two-third of usual one.

Davidson<sup>4)</sup> observed from his results obtained by the modified gas-flow method that, though the beginning point of the plastic state was independent of the rate of heating, the maximum resistance as well as the end point of the plastic state became higher with the acceleration of that rate. The same results were obtained by Roga<sup>5)</sup>.

It was recognized by using a Gieseler plastometer<sup>6)</sup> that the fluidity as well as the plastic range considerably increased with the rise of resolidification temperature when the heating rate rose, in spite of the almost constant softening temperature.

Table 2 records some results obtained by a modified Gieseler plastometer on the coals denoted in table 1. Changing states of the maximum fluidity due to a variation of the rate of heating are illustrated in Fig. 1. In these cases, the maximum fluidity as well as the temperature of fusion, of maximum fluidity and of the resolidification rise with the acceleration of the rate of heating,

TABLE 1.

Sample Coal	Proximate Analysis				Elementary Analysis				
	Mois.	Ash	V. M.	F. C.	C	H	N	S	O
Yubari	1.48	13.56	39.88	45.08	81.91	5.37	3.15	0.36	9.21
Mayaji	2.10	13.76	39.84	44.30	73.48	6.31	3.46	0.26	16.49
Imported Coal (S)	1.84	6.44	22.38	69.34	87.35	4.42	3.10	0.72	4.42

TABLE 2. Plastic properties at the various rates of heating.

Sample Coal	Rate of Heating	Soft- ening Temp. °C	Fusion Temp. °C	Maximum Fluidity Point		Resolidifi- cation Temp. °C	End- Point Temp. °C	Plastic Range °C
				Temp. °C	Fluidity Div./Min.			
Yubari	2.5	364	403	431	44,700	455	463	52
	5.0	365	412	444	52,000	478	493	66
	7.5	365	420	462	55,500	488	500	68
Yubari + 30% of Coke	2.5	362	408	439	22,094	459	472	51
	5.0	364	419	441	42,850	476	487	57
	7.5	366	420	448	54,510	482	492	62
Mayaji	2.5	362	408	439	22,094	459	472	51
	5.0	364	419	441	42,850	476	487	57
	7.5	366	420	448	54,510	482	492	62
Imported Coal (S), weathered	2.5	384	429	446	117	459	475	30
	5.0	399	445	465	390	481	500	36
	7.5	400	449	471	545	481	501	32
Imported Coal (S)	2.5	390	426	442	715	464	474	18
	5.0	392	443	470	1,830	491	505	38
	7.5	390	447	472	3,580	497	512	50

as has been shown by other researchers.

It should be considered to be a factor in the raising of these temperatures that the more rapid the rate of heating, the larger is the difference between the net temperature of coal in the retort and that in the metal bath where the temperature is measured.

It has been stated that the temperature at which volatile matter is expelled at the maximum rate, was also transferred to the higher side, when the rate of heating became faster, and the temperature of

primary decomposition of the coal substance occurred in the early period of the plastic state<sup>9</sup>. These results suggest evidence relating to a close relation between primary thermal decomposition and the formation of the plastic state in bituminous coal, as has been described by Mott and Wheeler<sup>7</sup>.

On these changes of plastic properties, Gieseler<sup>8</sup>) said that the temperature interval of the remaining of tar on the residual coal when rapidly heated, was so long as to promote the developing of the plastic state. On the other hand, Brewer<sup>10</sup>) maintained that the rate of formation of the plastic materials was accelerated by a rapid rate of heating.

An increase in tar yield by the rapid heating was reported by Warren<sup>10</sup>) in whose experiments the change of gas components also happened at the rapid rate of heating, especially during the pre-plastic range. A hypothesis relating to these results was offered by Warren. According to it, the increase of tar yield would depend on the idea that the molecules depolymerized at the lower temperature range, might become larger ones by a condensing reaction in the sensitive range which meant the preplastic state. When rapidly heated, especially during the sensitive range, the time available for condensation in the interval is shorter than that

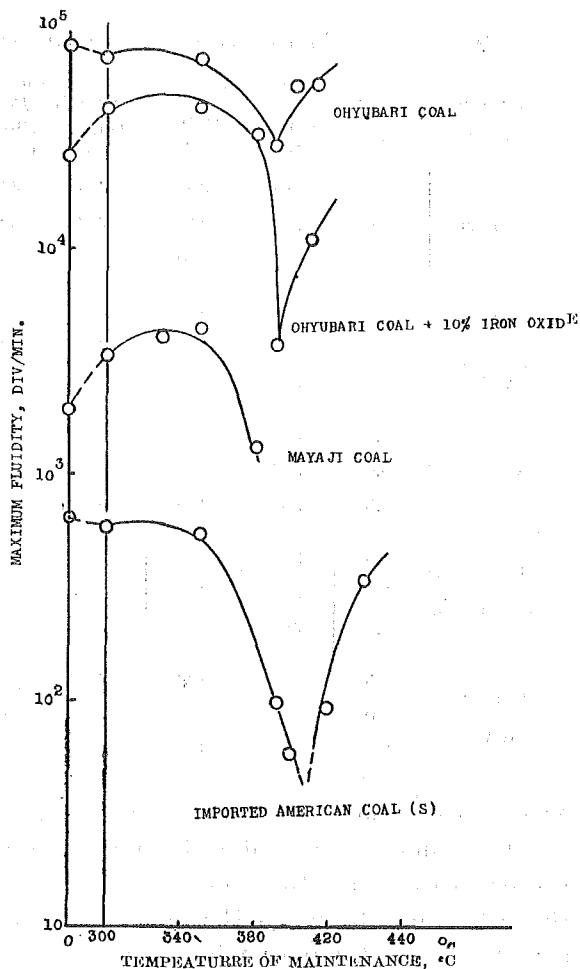


Fig. 2. Maximum fluidity of coals maintained at various temperatures for one hour while measurements were being carried on by a Gieseler plastometer.

at the slow rate of heating. Hence the increase of tar yield at the rapid rate of heating was attributed to a less number of the large molecules formed by the condensation in the sensitive range. The same idea was described by Fieldner<sup>11)</sup>.

Fig. 2 shows the maximum fluidity of the coal samples which were heated up to the various temperatures and then maintained at those temperatures for one hour while measurements were being made by the plastometer.

Some increases in the fluidity are found on the maintaining at the temperatures, 300°C to 350°C, in Yubari as well as in Mayaji coal. Remarkable decreases appear above 370°C to reach the minimum values at the temperature of the beginning of the plastic state above which the decreases diminish rapidly as the maintained temperature rises further. This result will be explained easily by Warren's theory relating to the increase of tar yield: the increase of fluidity between 300° and 350°C may be attributed to the depolymerization (or peptisation) of the coal constituents at this temperature range.

These facts lead one to believe that the thermal changes of coal constituents in the low temperature range below the plastic state, should be considered important factors relating to the plastic properties. Parr<sup>12)</sup> has emphasized that the thermal reaction of coal substance below the softening temperature should have been noticed as a conditioning stage in the carbonization, and should have been as interesting as the time factor.

It will be easily realized that the lower limits of temperature of the treatment by which the caking power is affected, should depend upon the kind of coal. Longchambon<sup>13)</sup> recognized no effect of 105°C on a coal, Schläpfer<sup>14)</sup> observed a decrease of the caking power due to heating at 150°C for 20 min. and its perfect destruction when heated at 200° to 250°C for 15 to 20 min.

Audibert<sup>15)</sup> reported that there was no appreciable effect below 350°C but that there was so large effect at 350°C that the caking power was perfectly destroyed by heating for 4.5 hr.

Interesting results relating to such thermal changes of the coal constituents in the low temperature range, were published by Bunte<sup>16)</sup>, who carried on pyridine-extraction at 50°C on Saar Gas Coal "Heinitz" (V. M. 34.5%, Ash 1.9%, Moist. 1.3%: C 85.4%, H 5.5%, O+N 8.3%, S 0.8%), passed through 400 mesh, which was heated in a silica tube in vacuum in a metal bath which had already been heated up to the

required temperatures as high as 400°C.

In the present author's laboratory, too, samples of Yubari coal, passed through 65 mesh, were heated up to various temperatures below 450°C at the rate of heating, 2 to 20°C/min. and then were extracted with pyridine and benzene by a Soxhlet apparatus, respectively.

TABLE 3. Results on Yubari coal heated at various rates of heating.

(1)

Maximum temperature °C	Rate of heating °C/min	Increased weight of		Gas vol. evolved c.c.	Weight loss %	Extracted amount with		Dispersed* humins %
		active charcoal %	calcium chloride %			benzene %	pyridine %	
250	2	0.30	0.49	0	0.78	7.2	20.2	13.0
300	2	0.37	0.49	0	0.87	7.6	20.2	12.6
350	2	0.37	1.05	0	1.68	3.0	19.6	16.6
375	2	1.21	1.15	15	2.26	2.7	20.2	17.5
400	2	1.27	1.26	28	2.60	2.0	27.3	25.3
425	2	1.43	3.80	115	5.70	2.9	31.3	28.4
250	5	0.34	0.22	0	0.96	11.8	22.3	10.5
300	5	0.56	0.72	0	1.44	7.3	22.5	15.2
325	5	0.64	0.87	0	1.50	3.0	23.5	20.5
350	5	0.95	1.04	7	1.91	3.9	24.0	20.1
375	5	0.95	1.35	13	2.50	3.2	25.0	21.8
400	5	0.18	1.49	52	2.60	3.3	31.0	27.7
425	5	1.15	2.07	61	3.13	3.5	32.5	29.0
450	5	1.30	3.40	110	4.69	3.4	33.0	29.6
250	12	0.00	0.49	0	0.56	5.4	20.3	14.9
300	12	0.02	1.01	0	1.12	7.2	20.7	13.5
350	12	0.64	0.85	5	1.44	7.8	21.0	13.2
375	12	0.90	0.96	10	1.70	7.5	24.4	16.9
400	12	0.89	1.46	27	2.75	7.0	29.5	22.5
425	12	0.01	1.50	33	3.00	4.0	27.0	23.0
250	20	0.00	0.87	0	0.80	1.7	18.3	16.5
300	20	0.01	1.05	0	1.15	2.8	17.8	15.0
325	20	0.83	0.95	3	1.85	3.7	18.5	14.8
350	20	1.05	1.13	3	2.20	9.5	23.0	13.5
375	20	1.14	1.51	25	2.45	9.6	25.0	15.4
400	20	1.32	1.65	36	3.25	9.0	29.4	20.4
425	20	2.34	2.26	140	5.75	8.4	34.0	25.6
—	—	—	—	—	—	4.0	21.2	17.2

( 2 )

## Results on Yubari maintained at various temperatures.

Maintaining		Increased weight of		Gas vol. c.c.	Weight loss %	Extracted amount with		Dispersed* humin %
temp. °C	time hr.	act. char. %	CaCl <sub>2</sub> %			benzene %	pyridine %	
250	1	0.04	1.12	0	1.14	6.2	21.8	15.6
250	2	0.06	1.30	0	1.21	4.8	21.7	16.9
250	3	0.11	1.32	0	1.30	4.5	19.3	14.8
300	1	0.50	1.29	0	1.85	5.6	20.6	15.0
300	2	0.50	1.33	0	1.89	4.6	19.4	14.8
300	3	0.65	1.44	0	1.97	4.4	19.2	14.8
350	1	0.11	2.62	10	3.06	6.8	23.6	16.8
350	2	0.85	3.64	60	4.86	6.9	23.8	16.9
350	3	1.26	4.08	88	5.47	7.2	24.0	16.8
400	1	1.23	3.96	58	5.42	8.5	30.5	22.0
400	2	1.66	4.15	89	5.97	8.4	28.9	21.4
400	3	1.76	4.20	115	6.15	9.6	25.7	18.1

\* Dispersed humin : Difference between amounts of pyridine- and benzene-extract.

The results are given in table 3, which includes the results obtained on the coals maintained at the temperatures, 250° to 400 °C, for a few hours, after being heated up to these temperatures at the rate of 5 °C/min. Also see Figs. 3-4. The dispersed humin indicated in the table means the difference of amount between the pyridine- and benzene-extract.

In these cases, all the pyridine-extracts considerably increased above 350°C. The dispersed humins decrease up to 350°C and then increase as much as the increase in pyridine-extract, excepting that of the extract at 5°C/min. which decreases up to 250°C and then increases. These decreases of the dispersed humins at 2° and 5°C/min. as shown below 350 °C, are to be attributed to the increases of the benzene-extracts, because the results show no appreciable change in the amount of pyridine-extract. This probably indicates that the increasing amount of the benzene-extract up to 250°C may be due to the conversion of a portion of the pyridine-extract to the benzene-soluble fraction owing to liquation or peptisation by the thermal action. The decrease in the benzene-extract as shown above 250°C may be attributed to a condensation in the fraction by which a portion of the fraction is converted



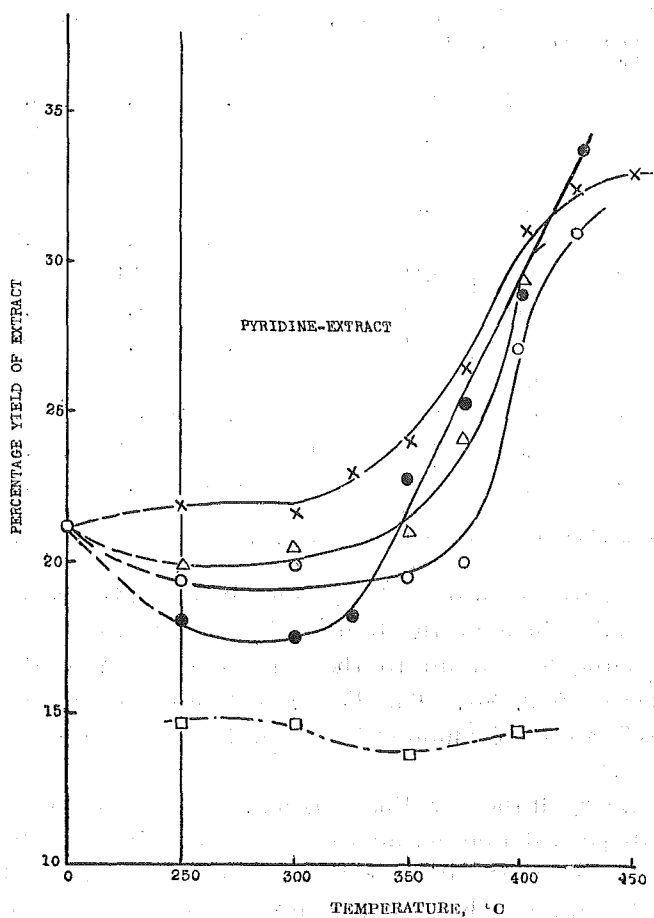


Fig. 3 a. Benzene- and pyridine-extract of Yubari coal heated up to different temperatures at various rates of heating.

—●— 2°C/min.      —○— 20°C/min.  
 —x— 5 "          —□— Bibai coal at 5°C/min.  
 —△— 12 "

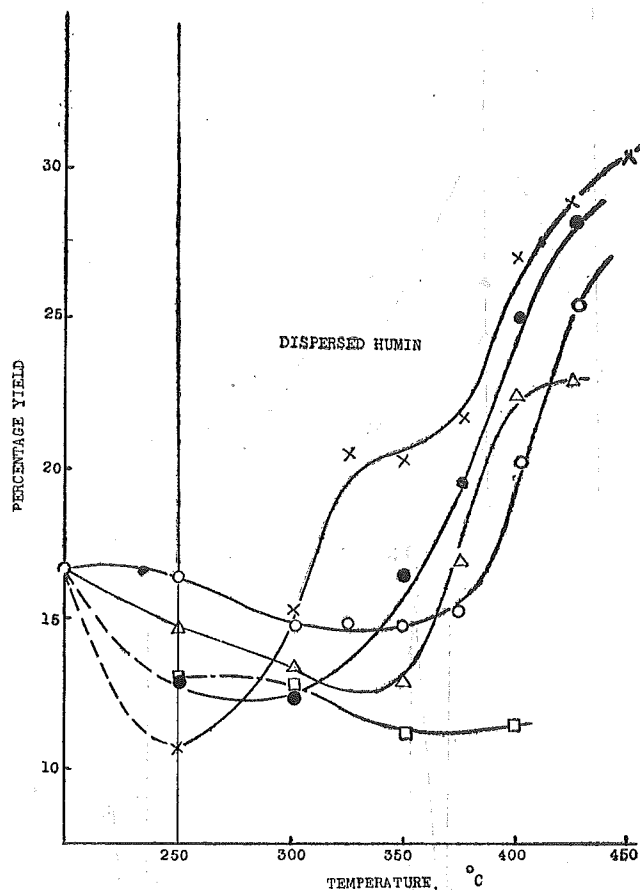


Fig. 3 b.

to be insoluble in benzene. In Fig. 4, the decreasing amount of the benzene-extract when temperature is maintained at 250°C for a few hours, suggests a possibility of the condensing reaction in the benzene-soluble fraction at this temperature. The amount of benzene-extract at the rate of 2°C/min. is less than that in the rate of 5°C/min. in Fig. 3. This may, therefore, be attributed to the slower passing through such temperature range in which the condensation is most active.

The amount of pyridine-extract decreases with the duration of the maintaining time at 250° and 300°C, and is almost constant at 350°C, cf. Fig. 4. In the temperature range, 250°C to 300°C, therefore, it is supposed that a condensation of the pyridine-extract to form larger

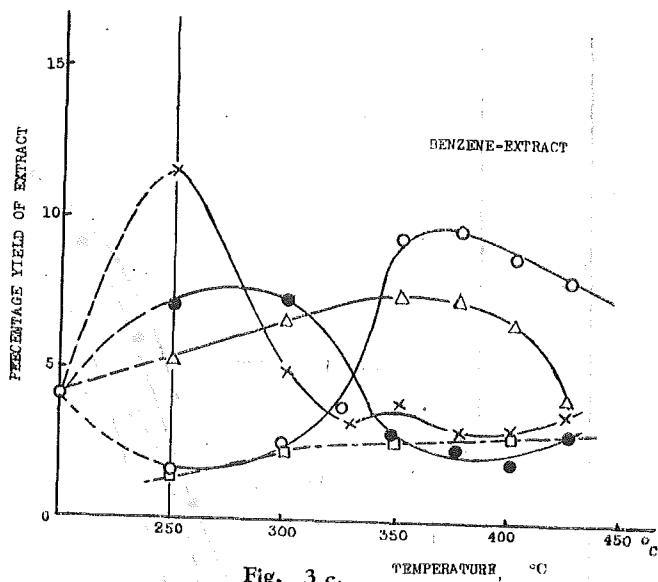


Fig. 3 c.

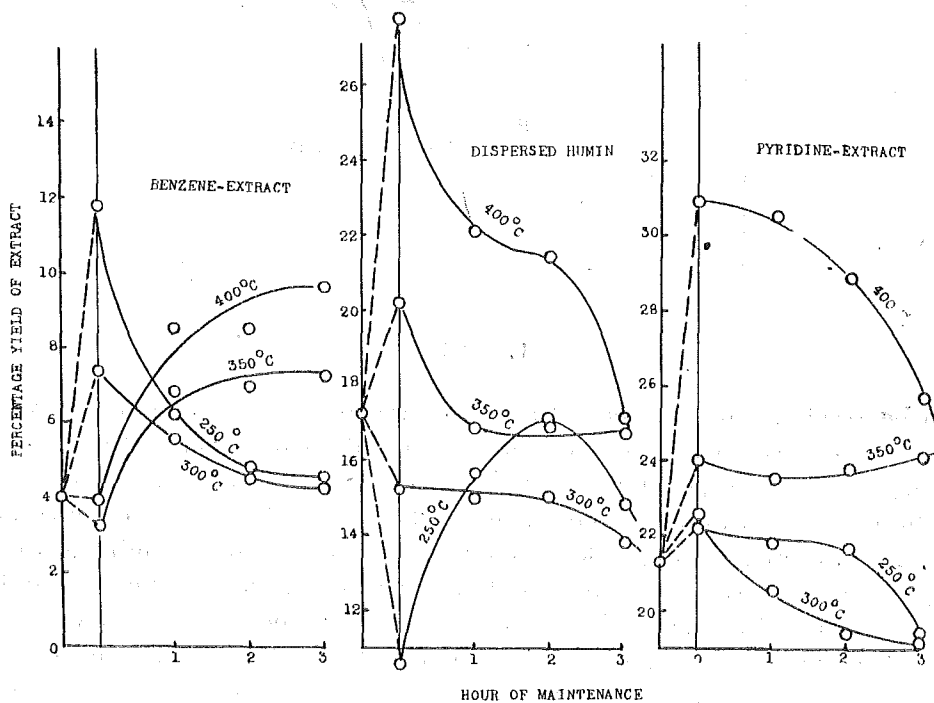


Fig. 4. Benzene- and pyridine-extract of Yubari coal maintained at 250° to 400°C for different hours after had reached to these temperatures at the rate of 5°C/min.

molecules is very active. This action was recognized as a polymerization by Bunte. It is, however, evident from the results shown in Fig. 4, that the condensation is of very slow velocity in such a coal as Yubari coal with high fluidity and high volatile-matter.

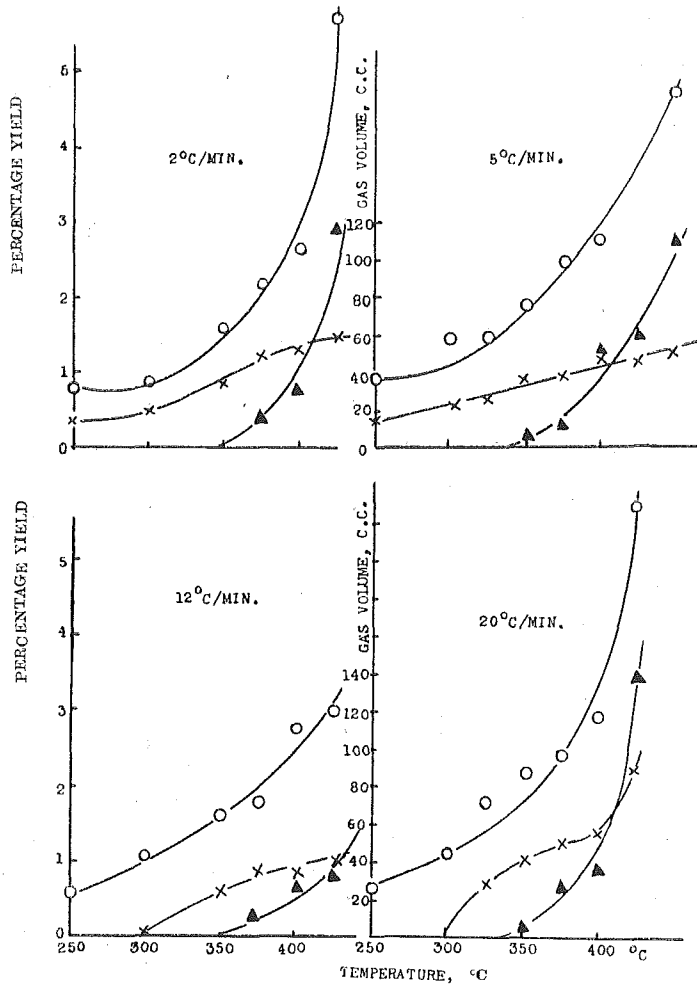


Fig. 5 Weight loss, increased weight of active charcoal used to absorb tar vapour, and gas volume evolved in the heating of Yubari coal up to different temperatures at various rates of heating.

- Weight loss.
- ×— Increased weight of active charcoal.
- ▲— Gas volume, c. c./20 gr.

According to the results shown in Fig. 5 (in which there are shown weight loss, volume of gas evolved, and increased weight of the active charcoal used to absorb oil vapour), in the carbonization at those rates of heating, this condensation is evidently never followed by any thermal decomposition to evolve gas, but seems to be of such a sort as to follow after dehydration, because  $H_2O$  alone is expelled from the coal in this temperature range.

It will be, hence, a reasonable idea that the condensation in coal constituents in the low temperature range, should be a reaction occurring between the molecules with outer-groups containing oxygen, due to dehydration.

Moreover, the amount of pyridine-extract somewhat increases above  $300^\circ$  to  $350^\circ C$  at the rate of  $5^\circ C/min.$ ; it does not decrease, rather tends to increase a little during the maintenance at  $350^\circ C$ . In this temperature range, therefore, it is probable that a sort of depolymerization or peptisation in the coal constituents may occur as described by Bunte<sup>(9)</sup> and Warren<sup>(10)</sup>. The increase of fluidity caused by the maintenance of temperature for one hour at  $300^\circ$  to  $350^\circ C$  (as in Fig. 2) may depend upon this action in the coal.

During the maintenance above  $350^\circ C$ , the amount of pyridine-extract as well as of dispersed humin, decreases, and on the contrary, that of the benzene-extract increases. Owing to the evolving of gas above  $350^\circ C$ , these actions must be attributed to the thermal decomposition of coal constituents to form larger and smaller molecules due to fissions and condensations.

Hence it again appears that the chemical changes of the coal constituents in the temperatures below the plastic state should be recognized as important in respect to the caking power.

An appreciable increase of the pyridine-extract as well as of the dispersed humin above  $350^\circ C$  does not appear in the heating of Bibai coal which is non-caking, in contrast with the considerably increasing amount in case of Yubari coal which has high fluidity. This difference should be noticed as a factor to explain the difference in coal constituents between the caking and non-caking coal. What the amount in Bibai coal hardly increases, must be due to the large development of condensation following dehydration, because of high oxygen content of the coal, and this fact must have a connection with undevelopment of the plastic state.

### Relation between the plastic state and the thermal decomposition.

It appears that the benzene-soluble portion upon the heating of coal alone does not directly take part in the developing of plastic state, from the results shown in Fig. 3; the maximum amount of benzene-extract in the heating of 2°C/min. and 5°C/min., occurs at 300° and 250°C, respectively, which are below the temperature of plastic state, and also that of decomposition. Hence the increase of dispersed humin following the thermal decomposition of coal constituents would be accepted as a factor relating to the development of plastic state. Being exactly true, this idea tends to disprove the isocolloid theory connected with the plastic state as described by Lahiri<sup>17)</sup>.

Fig. 6 gives the changing state of the fluidity in Yubari coal maintained for one hour at plastic state temperatures during the measurement. The maintained temperatures were 390°, 395°, 400° and 410°C, the coal mixed with 10% of iron oxide was also used.

At the beginning of the maintaining period, in all cases, the fluidity increases without interruption. This seems partially to be due to the rising of coal temperature in the retort, after the temperature rise in the metal bath was interrupted. When maintained at 400° and 410°C, the fluidity decreased in the later part of the procedure, but increased again with the rising of the temperature after the period of controlled maintaining had finished.

The decrease of fluidity in the later part of the maintaining period must be attributed to condensing reactions occurring in the thermal decomposition of the coal constituents, as shown by the decrease of pyridine-extract as well as that of dispersed humin during maintenance at 400°C, see Fig. 4. According to the rising of fluidity after the period of temperature maintenance, it appears that so small molecules as to be the dispersing constituents to develop the fluidity, are formed by further thermal decompositions of the coal constituents not reacting yet. Hence it is evident that constituents with different thermal stabilities exist in the coal; especially, this would be evidenced from the result in the maintaining at 410°C of the coal mixed with iron oxide where the fluidity appears again with the rising of temperature after it had almost disappeared at the end of maintenance period.

The decreases of fluidity during the maintenance period as well as of the maximum fluidity of the coal when mixed with iron oxide,

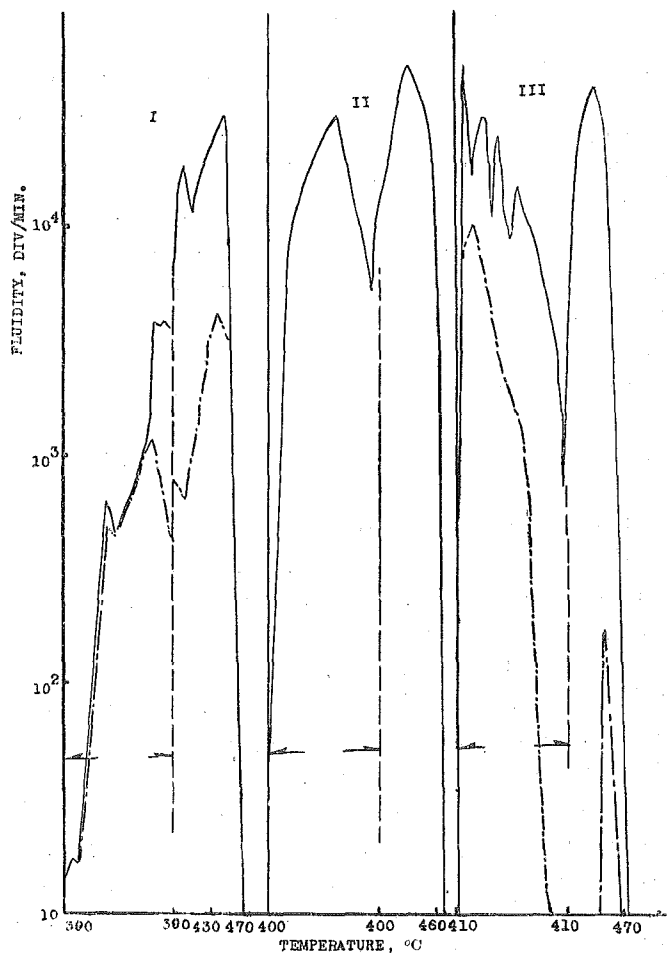


Fig. 6 Changing state of fluidity of Yubari coal maintained for one hour at different temperatures in the plastic state during the measurement of fluidity.

- |     |                                  |
|-----|----------------------------------|
| I   | Maintaining temperature of 300°C |
| II  | " " 400 "                        |
| III | " " 410 "                        |
- Yubari coal alone.  
 - - - - - Yubari coal mixed with 10% of iron oxide.  
 ← ————— Maintaining period.

are larger than those of the coal alone. It is, therefore, supposed that the condensing reaction in the coal constituents which prevents fluidity, may be accelerated by the presence of iron oxide.

Riley<sup>18)</sup> has reported from his X-ray study on chars, that the primary action of the admixture of inorganic compounds was the formation of nuclei around which the aromatic condensation could occur.

There is, however, a problem remaining viz., whether or not the condensation in coal constituents due to dehydration in the low temperature range is affected by the admixing of iron oxide. Moreover, another question arises whether the condensation in the plastic state is only one of aromatic condensation to develop the turbostratic graphitic structure, or whether another kind of condensation occurs simultaneously. These problems will be discussed later.

#### Decrease of the caking power due to oxidation.

It is well known that the caking power of oxidized coal decreases with the extent to which oxidation proceeds. Several theories relating to the reason therefor have been published.

Mott<sup>3)</sup> maintained that the decrease depended upon the diminishing of wettability of the coal surface by "oil", which covers pores in the coal to develop pressure an account of to confine gas evolved in the pores. Yohe and Harman<sup>19)</sup> recognized the wettability of oxidized coal by water as being larger than that of unoxidized coal. Karavaew<sup>20)</sup> supposed that the large hygroscopicity of oxidized coal would be attributed to increases of OH, CO and COOH groups in the coal constituents by oxidation. Hence it appears that the wettability of coal by oil decreases with oxidation.

There is, however, a question of whether or not the oil which is recognized as ether-soluble fraction by Mott<sup>3)</sup>, is hard enough to make up the pressure to create the surface-flow of the molecules around the pores.

Berkowitz<sup>2)</sup> has explained the intumescence mechanism according to the factors as follows:

1. the pore volume of the coal and the size of local constrictions which it contains.
2. the amount of potentially volatile matter that must be disengaged from the coal in the critical temperature interval, i.e., the



intumescence range.

3. the size and shape of the escaping molecules.

On the results in which the collapse of the pore structure of a coal in the plastic range was so limited that the structural units of the coal retained their identity, Berkowitz explained that the softening of coal was attributable to certain internal rearrangements of coal molecules, which would be restricted to the two dimensions as observed in some micellar polymers.

However, it appears that the presence of highly viscous liquid constituents in the plastic range can not be denied on account of the facts as follows:

1) the coal having as high volatility and fluidity as Yubari coal, when heated in a tube to determine the swelling power of coal particles layer, exhibits a boil in the plastic range.

2) the large pressure developed in the oven when the medium or low volatile coking coal is carbonized, indicates very great impermeability of the plastic layer to the gas disengaged from the coal in the lower temperature side. Hence it appears that there is almost no room among the coal particles in the plastic state.

Berkowitz stated that the decrease in the caking power caused by oxidation appeared to be mainly due to an opening of the pore structure of the coal because the required increase in heat of wetting and porosity had actually been observed experimentally in the oxidized coal.

In Shinmura's results<sup>21)</sup>, the caking power was considered to be related to the amount of  $\gamma$ -fraction and of the oxygen in  $\alpha$ -fraction. This elucidates one role of the oxygen in the coal substance as an important factor with respect to the caking power.

Additionally to the above, there is a theory relating to the non-caking of oxygen-rich coal by which the non-development of the plastic state in it must be attributed to such a large intermicellar force in coal micelles that the softening of it becomes difficult on account of the slight mobility of the micelles.

The fluidity of Yubari coal, which had been oxidized by air, nitric acid and electrolysis, were measured in this study. The oxidation by air was carried out at 94° to 96°C in a glass tube, charged with 10 gr. of sample coal, immersed in a water bath, through which air was passed at the rate of 300 c.c./min.

Deoxygenation by hydrogen also was done in the same apparatus.

The oxidations with nitric acid and electrolysis were at 30°C in a thermostat, and the electro-reduction also was carried out at the same temperature. In the electrolysis the current density was 0.3 A/cm<sup>2</sup>. These results are recorded in table 4 and Figs. 7-8.

TABLE 4.

(1)

Results obtained from air oxidation.

Sample No.	Oxidation		Weight loss %	Products		Consumed oxygen %	Oxygen fixed on coal %
	temp. °C	time hrs.		H <sub>2</sub> O %	CO <sub>2</sub> %		
0-1	94	3	- 0.19	0.54	0.51	1.12	—
0-2	95	5	0.70	0.89	1.03	1.24	33.0
0-3	95	8	0.85	1.25	1.08	1.38	—
0-4	96	10	0.86	1.38	1.12	1.40	39.3
0-5	96	15	1.85	1.80	1.58	1.45	46.9
0-6	96	16	2.06	1.82	1.63	1.47	—
Sample		Elementary analysis (Dry, ashless)					
		C	H	O + S	N		
Yubari		86.3	6.1	1.5	6.1		
0-2		86.1	6.1	1.4	6.4		
0-4		85.2	6.0	1.4	7.4		
0-5		85.4	6.0	1.3	7.3		

(2)

Results of oxidation by Nitric acid.

Sample No.	Oxidation time hrs.	Weight loss %	Elementary analysis			
			C	H	N	O + S
N-0-1	1.5	2.04	84.6	6.1	1.4	7.9
N-0-1	3	5.70	84.5	5.9	1.5	8.1
N-0-1	6	6.58	84.6	5.7	1.7	8.0

(3)

## Results of anodic oxidation.

Sample No.	Oxidation time hrs.	Weight loss %	Elementary analysis			
			C	H	N	O + S
E—0—1	8	4.02	84.3	5.9	1.1	8.7
E—0—2	16	7.76	84.6	5.7	1.2	8.5
E—0—3	32	9.51	85.0	5.6	1.3	8.1

(4)

## Results of hydrogen reduction.

Sample No.	Sample reduced	Catalyst	C	H	N	O + S
HR—1	0—2	used	87.5	6.1	1.2	5.2
HR—2	0—4	"	85.3	6.2	1.3	7.2
HR—3	0—5	none	87.3	6.4	1.3	5.0

(5)

## Results of cathodic reduction.

Sample No.	Sample reduced	Elementary analysis			
		C	H	N	O + S
ER—1	N—0—1	87.5	6.6	1.4	4.5
ER—2	N—0—2	85.4	6.3	1.5	6.8
ER—3	N—0—3	86.1	5.9	1.6	6.4
ER—4	E—0—1	84.5	6.2	1.2	8.1
ER—5	E—0—2	85.0	6.0	1.3	7.7
ER—6	E—0—3	86.3	5.8	1.4	6.5

(6)

## Plastic properties of the coals.

Sample	Softening temp. °C	Fusion temp. °C	Maximum fluidity		Resolidification temp. °C	End point temp. °C	Plastic range °C
			temp. °C	fluidity			
Yubari	356	403	429	83.400	456	464	53
0—1	367	406	430	34.200	458	466	52
0—2	365	405	430	28.500	455	464	50
0—3	370	410	430	26.900	456	464	46
0—4	370	409	430	26.000	456	467	47
0—5	376	414	431	6.350	450	462	36
E—0—1	375	404	430	2.180	450	459	46
E—0—2	375	420	432	660	444	459	24
E—0—3	392	428	431	70	441	458	17
N—0—1	362	404	429	58.200	460	470	56
N—0—2	370	405	429	29.800	456	465	51
N—0—3	370	404	430	20.700	454	463	50
HR—0*	367	412	432	13.250	458	467	46
HR—1	375	421	431	360	448	460	27
HR—2	362	417	430	840	441	454	24
HR—3	367	409	431	4.900	451	458	42
HR—4*	365	413	432	8.830	456	465	43
HR—5*	367	419	431	375	439	451	20
ER—1	360	409	432	32.100	456	469	47
ER—2	375	421	429	112	436	454	15
ER—3	335	—	431	42	—	454	—
ER—4	380	415	432	18.750	451	465	36
ER—5	375	411	432	9.100	451	463	42
ER—6	374	414	434	15.780	462	473	48
Yubari-1*	358	404	432	71.500	458	467	54
Yubari-2*	360	417	432	360	446	461	29

\* HR—0; sample 0—1 reduced by hydrogen without catalyst.

HR—4; sample 0—3 reduced by hydrogen without catalyst.

HR—5; sample 0—5 reduced by hydrogen with 5% of catalyst.

Yubari—1; Yubari coal reduced by hydrogen without catalyst.

Yubari—2; Yubari coal reduced by hydrogen with 5% of catalyst.

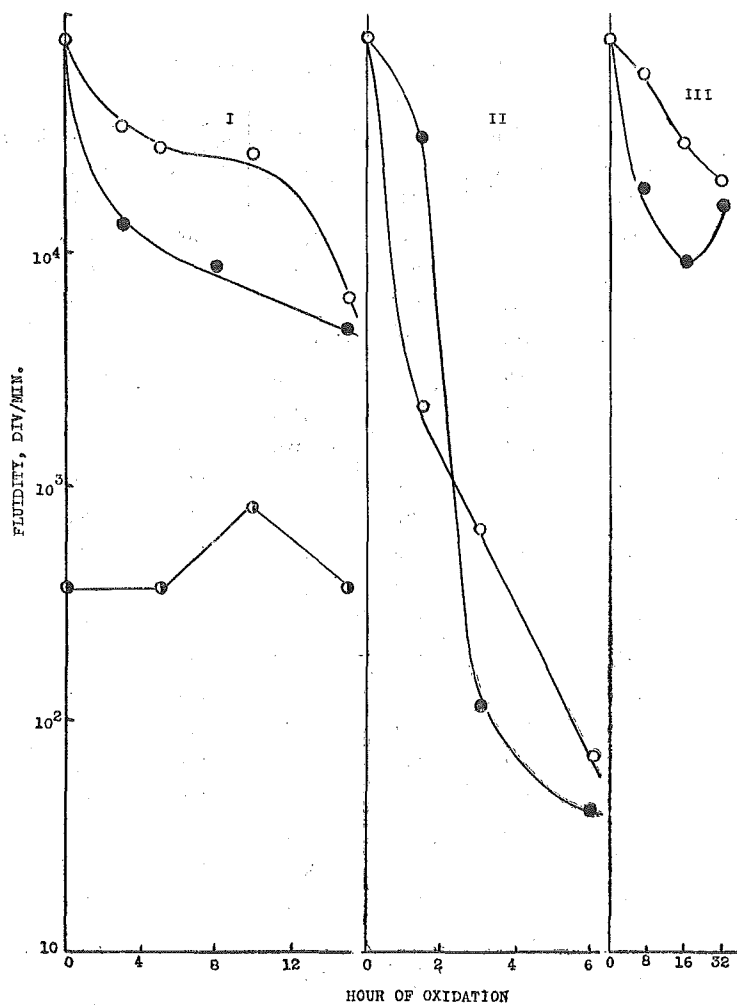


Fig. 7. Maximum fluidity of Yubari coals oxidized for different hours by various methods and of those coals after deoxygenated by hydrogen at about 100°C or cathodic reduction at 30°C.

- I { ○ Coal oxidized with air at about 96°C.  
 ● Same coal deoxygenated with hydrogen at 100°C in presence of catalyst after oxidation.  
 ● Same coal deoxygenated without catalyst.
- II { ○ Coal oxidized with nitric acid at 30°C.  
 ● Same coal deoxygenated by cathodic reduction after oxidation.
- III { ○ Coal oxidized by anodic oxidation at 30°C.  
 ● Same coal deoxygenated by cathodic reduction after oxidation.

1. *Relation between the fluidity and oxygen content.*

As exhibited in Fig. 7, the fluidity in all oxidized coals is lower than that in the original coal, especially the lowering in the coal oxidized with nitric acid is very much greater than that in other oxidized coals. The fluidity of the coals deoxygenated after the oxidations also is of lower value than that of the oxidized coals themselves, excluding that of the coal reduced by electrolysis after being oxidized in 10% nitric acid for 1.5 hr.

On the other hand, the oxygen in the coals in which oxygen increased appreciably, decreases corresponding to the extent of reduction; cf. Fig. 8. Hence it appears that no relation is observable between the oxygen content itself and the fluidity in these coals, just as has

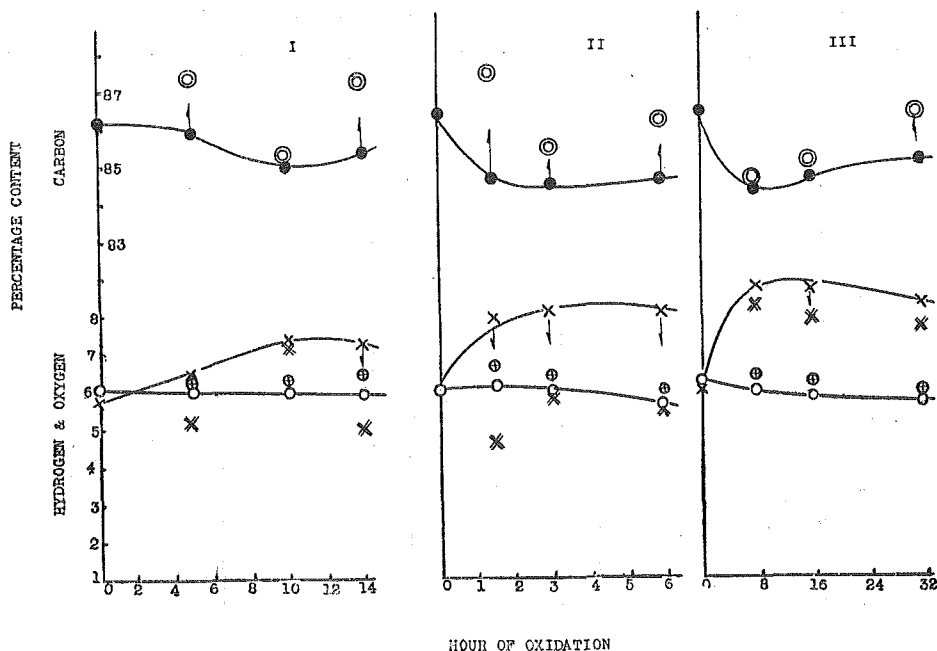


Fig. 8. Elementary composition of oxidized Yubari coals and of those coals after deoxygenation.

I. Coals oxidized with air about 96°C.

II. " " with nitric acid at 30°C.

III. " " with anodic oxidation at 30°C.

● Carbon	} in oxidized coal.	⊙ Carbon	} in same coal after deoxygenation.
○ Oxygen		⊕ Oxygen	
× Hydrogen		⊗ Hydrogen	

been reported by Rose and Sebastian<sup>22)</sup>. In their results, no relation was present between agglutinating values and oxygen contents when a coal was oxidized.

It will, therefore, be supposed that the decrease of the caking power does not depend on the increased oxygen itself in the oxidized coal, but rather on the change to which the coal constituents submit in the oxidation; this throws doubt upon the intermicellar theory by which the strengthening of intermicellar force due to the increased oxygen by oxidation is considered to prevent development of the plastic state.

Fig. 9 gives the results of the elementary analyses of the coals heated up to 450°C. Sample coals were Yubari, its oxidized samples and Kakuta non-caking coal.

In these materials, the deoxygenating degree in the coal oxidized by air for 15 hrs. is appreciably lower than that of other coals. It may

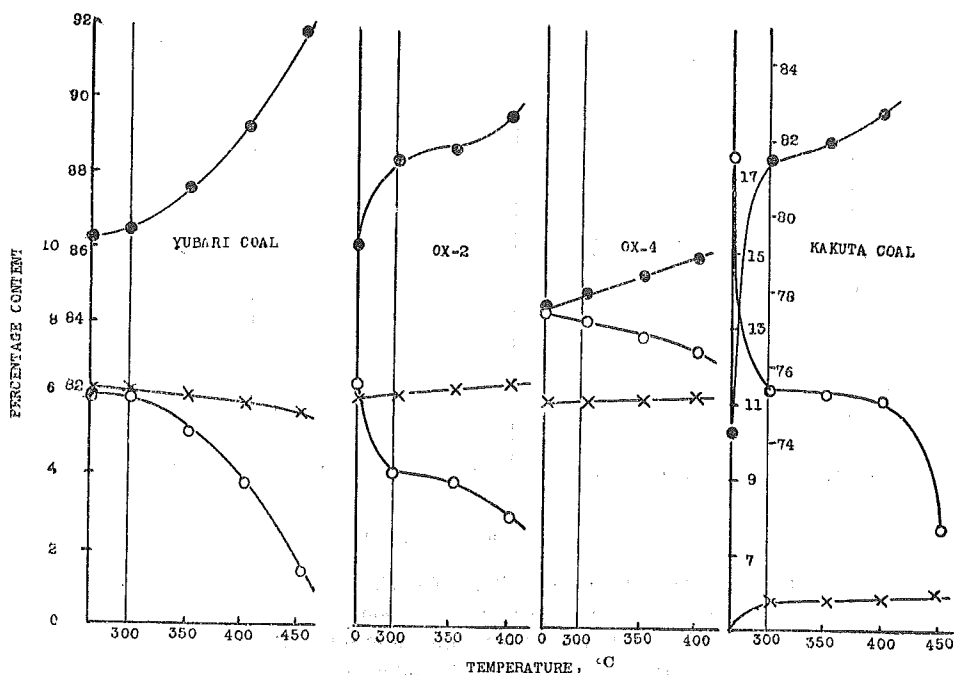


Fig. 9. Elementary compositions of Yubari coal, its oxidized coals, and of Kakuta coal heated up to different temperatures at the rate of 5°C/min.

● Carbon. ○ Oxygen. × Hydrogen.

be attributed to the relatively great stability of the oxygen in the coal on account of the long oxidation time. The oxygen content at 400°C of the coal oxidized for 5 hrs., on the contrary, is a little less than that of original coal, in spite of its lower fluidity. Moreover, it is known according to Porter and Taylor's results<sup>23)</sup> shown in table 5 that most of the oxygen in the coal is expelled from it in the carbonization up to 450°C. The oxygen-carbon complex formed in a coal by oxidation decomposed to evolve CO<sub>2</sub>, CO and H<sub>2</sub>O at temperatures below that of decomposition<sup>24)</sup>. It has been recorded that the oxygen-carbon complex decomposed to evolve CO<sub>2</sub>, CO and H<sub>2</sub>O at 200°C in vacuum<sup>25)</sup>. Lefebvre and Faivre<sup>26)</sup> also confirmed that all the increased oxygen in an oxidized coal was nearly all removed as CO<sub>2</sub>, CO and H<sub>2</sub>O, when it was heated up to 350°C.

TABLE 5. Amounts of oxygen removed by heating up to 450°C<sup>23)</sup>.

Name of Coal	New River, West Virginia	Pittsburgh	West Frankfort, Illinois	Sheridan country, Wyoming
Moisture	0.60	0.93	2.07	5.93
Volatile matter	21.60	33.02	35.21	41.47
Ash	3.23	9.07	9.17	6.45
C	89.30	85.25	80.91	74.94
H	4.88	5.45	5.14	5.26
O	3.60	5.59	10.89	16.93
Volatile matter	22.42	36.69	39.70	47.35
Amount of oxygen removed, as	$\left\{ \begin{array}{l} \text{H}_2\text{O} \quad \% \\ \text{CO}_2 \quad \% \\ \text{CO} \quad \% \end{array} \right.$	2.00	3.80	7.37
		0.32	0.25	0.77
		0.12	0.13	0.34
Total	2.44	4.18	8.48	15.35
Deoxygenated percentage	70.6	83.1	8.48	100.3*

\* This error might be based on measurement of moisture in such a low rank coal.

Hence it appears that the change of coal constituents, as relates to the decrease of the caking power, must happen in the deoxygenating process, which occurs in the oxidation and carbonization following it; the condensation developed due to the increased oxygen should be



regarded as the factor to decrease the fluidity, the same as mentioned in the oxygen-rich coal respecting its non-caking.

2. *Amounts of the benzene- and pyridine-extract in the oxidized coal and when heated up to the plastic state.*

The results obtained by the pyridine- and benzene-extraction of oxidized Yubari coal are given in table 6, Fig. 10, and those of the coals heated up to various temperatures are also recorded in table 6

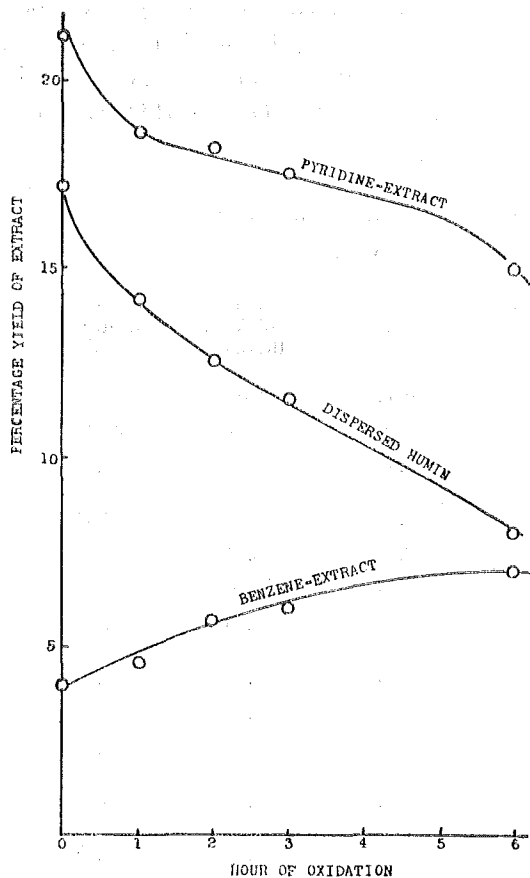


Fig. 10. Benzene- and pyridine-extract of oxidized Yubari coal.

extract from the oxidized coal was soluble in ammonia in spite of the insolubility of that from the original coal. These results show that there must be a change in the coal constituents due to the oxidation.

and Fig. 11. This oxidation was carried out at 150°C and 200°C by using an oil bath, sample coals, passed through 65 mesh, were used for these extractions.

Amounts of the pyridine-extract as well as of the dispersed humin decrease with the oxidation time, but contrariwise the amount of benzene-extract increases.

The amount of benzene-extract obtained by Fischer<sup>27)</sup>, when a coal had been oxidized at 110°C for 30 days, decreased from 7.5% to 0.03%. The amount of benzene-extract which increased in the present experiment up to 6 hrs., therefore, should decrease with further oxidation, as recorded by Fischer. In addition, Fischer reported an increase from 1.5% to 7.4% in the ethyl alcohol-extract by the oxidation.

In this case, however, the

TABLE 6. Results of the heating and extraction on oxidized Yubari coal.

Sample No.	Temp. of heating °C	Weight loss	Increased weight of		Vol. of gas evolved c.c.	Amount of extract with		Dispersed humin %
			active char, %	CaCl <sub>2</sub> %		benzene	pyridine	
Yubari	—	—	—	—	—	4.0	21.2	17.2
"	250	0.96	0.34	0.22	0	11.8	22.3	10.5
"	300	1.44	0.56	0.72	0	7.3	22.5	15.2
"	325	1.50	0.64	0.87	0	3.0	23.5	20.5
"	350	1.91	0.95	1.04	7	3.9	24.0	20.1
"	375	2.50	0.95	1.35	13	3.2	25.0	21.8
"	400	2.60	1.18	1.49	52	3.3	31.0	27.7
"	425	3.13	1.15	2.07	61	3.5	32.5	29.0
"	450	4.69	1.30	3.40	110	3.4	33.0	29.6
OX—1	—	—	—	—	—	4.6	18.6	14.0
"	300	1.44	0.21	0.39	8	7.2	17.9	10.7
"	350	2.30	0.24	0.83	17	8.9	18.7	9.8
"	400	3.24	0.36	0.90	26	9.0	20.6	11.6
OX—2	—	—	—	—	—	5.7	18.2	12.5
"	300	1.43	0.18	0.34	4	2.2	17.2	15.0
"	350	1.82	0.21	0.59	10	5.7	17.3	11.6
"	400	3.09	0.33	0.73	28	6.9	17.3	10.4
OX—3	—	—	—	—	—	6.0	17.6	11.6
"	300	1.31	0.17	0.33	5	1.1	14.3	13.2
"	350	1.81	0.20	0.55	10	1.2	14.6	13.4
"	400	3.04	0.29	0.71	27	1.3	15.1	13.8
OX—4	—	—	—	—	—	7.0	15.0	8.0
"	300	1.28	0.14	0.33	0	2.1	14.4	12.3
"	350	1.80	0.18	0.53	10	2.2	15.0	12.8
"	400	3.01	0.25	0.67	28	2.4	15.2	12.8
OX—5	—	—	—	—	—	7.0	11.7	3.7
"	300	1.08	0.07	0.30	0	2.1	12.9	10.8
"	350	1.88	0.10	0.54	15	2.4	13.8	11.4
"	400	2.98	0.25	0.58	30	2.6	14.8	12.2
Bibai	250	1.67	0.04	1.41	0	1.6	14.6	13.0
"	300	1.87	0.16	2.08	2	1.9	14.7	12.8
"	350	3.21	0.23	2.25	34	2.3	13.5	11.2
"	400	3.43	0.30	3.13	42	3.0	14.7	11.7

OX—1; Yubari coal oxidized by air at 150°C for one hour.

OX—2; " " " for 2 hrs.

OX—3; " " " for 3 hrs.

OX—4; " " " for 6 hrs.

OX—5; " " at 200°C for one hour.

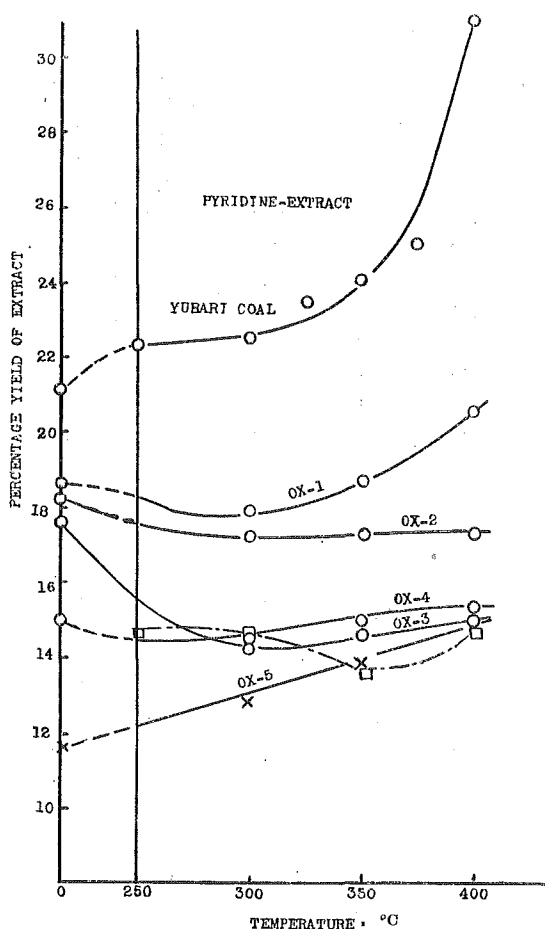


Fig. 11 a. Benzene- and pyridine-extract of Yubari coal and its oxidized coals heated up to different temperatures at the rate of 5°C/min.

—○— Yubari coal.  
 ·—□—· Bibai coal.

increasing amounts of the pyridine-extracts above 300°C decrease with the extent to which the coal was oxidized; the amounts in the coals so oxidized as to be non-caking, OX-3 and OX-4, are nearly similar with those in non-caking Bibai coal at temperatures above 300°C. These findings may be due to that condensation that occurred in the process of carbonization of the oxidized coal, which must be ascribed to the deoxygenation in the coal, as  $\text{CO}_2$ ,  $\text{CO}$ , especially  $\text{H}_2\text{O}$ . Hence it appears

It may be possible reasonably to conclude that the decrease in the pyridine-extract may be attributed to the strengthening of the intermicellar force due to the increased oxygen. There may not be such evidence as to deny this idea at the present time. But the increase in the amount of benzene-extract can not be explained by this idea only. Hence, it is also a reasonable consideration besides the idea mentioned above, that the decrease should be attributed to the enlargement of size of the coal molecules due to the condensation among them following with the deoxygenation as  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2\text{O}$  in the oxidation process. The increasing amount of benzene-extract in this experiment may be attributed to the fission of intramolecular bondings attending the oxidation.

In the oxidized coals,

as a reasonable conclusion that this decrease in the pyridine-extract, as seems to be true also of the dispersing humin in the plastic state, might be the direct cause of the lowering in the fluidity following oxidation.

On the other hand, the increases of benzene-extracts at temperatures above 300°C in case of the oxidized coal, OX-1 and OX-2, may be attributed to fissions of the intramolecular bonds, which occur in the oxidized molecules by the thermal action in the carbonization.

According to the result in which such oxidized coals, as OX-1 and OX-2, have lower fluidity than that in the original coal, in spite of their large amounts of benzene-extract at the initial stage of the plastic state, 400°C, it is

further recognized to be an interesting conclusion that so small molecules in the plastic temperature range as to be soluble in benzene, do not exert any appreciable effect on the caking power by themselves alone.

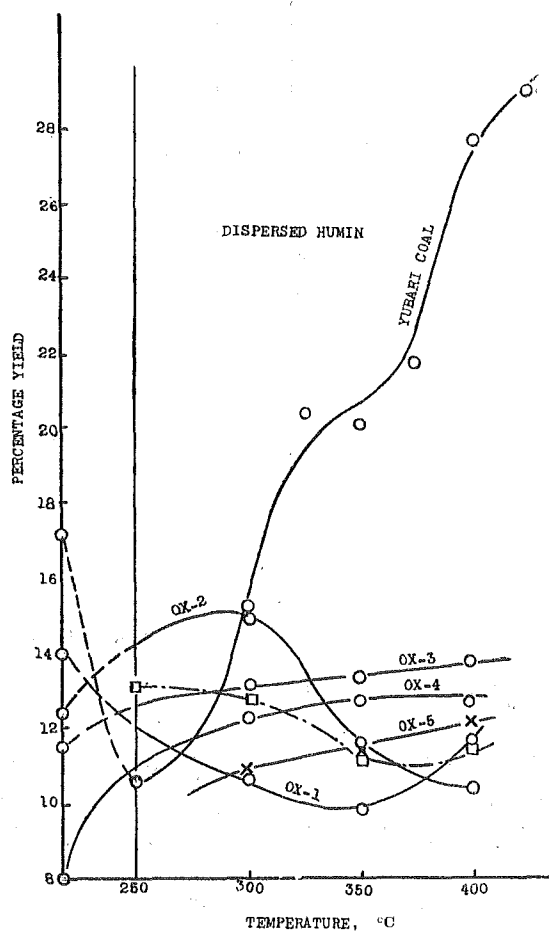


Fig. 11. b.

### 3. Other discussion of the condensation in the carbonization and oxidation process.

The decrease of tar yield in the carbonization at the slow rate of heating, was mentioned before; it has been observed also in the carbonization of oxidized coal. Schmidt<sup>(28)</sup> reported a sharp decrease of the

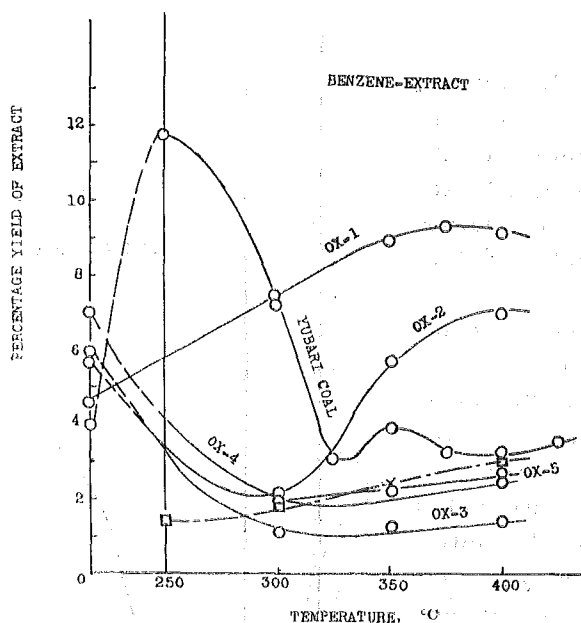


Fig. 11. c.

tar yield in the carbonization of oxidized coal and that the decrease was the most sensible indicator as to the extent to which the coal was been oxidized; the increase by 1% of the consumed oxygen in the oxidation matched a decrease of 16% in the tar yield, which corresponded with an increase of 0.3% in the coke yield. It should be of special interest that Warren explained the decrease of tar yield at the slow rate of heating, to development of the condensation in the sensitive range. Regarding Schmidt's results on the remarkable decrease of tar acids yield observed in the oxidized coal, it may appear that the decrease of tar yield in the oxidized coal also should be attributed to the condensation, which is related to the oxygen-containing outer-groups in the coal molecules formed in the oxidation.

It is known that when air is blown into the tar or oil in which pitch is dissolved, a certain condensation occurs to precipitate a sludge.

Pfeiffer<sup>20)</sup> stated that, when bitumen was oxidized at comparatively high temperatures (100° and higher), the scheme of the reaction was probably that high molecular constituents are dehydrogenated, water being formed, after which the dehydrogenated aromatic remnants condense to large molecules, finally to asphaltenes or, on prolonged oxi-

dation, to less soluble components (carbenes, carboids). When a bitumen was oxidized at 100°C, about 40% of the oxygen was converted into water and about 54% was combined in the bitumen. Chernozhukov and Krein<sup>30)</sup> reported particulars of the oxidizability of hydrocarbons in connection with their molecular structure; when aromatics with short side chains are oxidized, it is chiefly resins and asphaltenes that are formed. With increasing side chain length in the molecule the resin and asphaltene formation decreases and products of a more acidic character are formed. The role of oxygen in a polymerization, in general, has been recognized as an important factor, i. e., the polymerization of methyl acrylate at 100°C occurs only in the presence of air, and the same has been observed on vinyl acetate, or vinyl bromide.

Barnes<sup>31)</sup> reported that there occurred oxygen absorption and formation of peroxides in the interaction between enormous vinyl monomers and oxygen. The mechanism of polymerization as explained by Bawn<sup>32)</sup>, is the formation of peroxides and abstraction of hydrogen in molecules as a primary action to build up active radicals and the repetition of polymerization by branchings and cross linkings as a secondary reaction. The essential role of oxygen is to build up active free radicals to develop fissions as well as cross linkings.

When this mechanism is considered in connection with the oxidation of coal, the decrease of pyridine-extract would seem to be attributed to the cross linking, and the increase of benzene-extract to the fission.

Table 7 records the results of a study of the plastic properties of Yubari coal mixed with some organic and inorganic compounds. Sulphur has the greatest effect in preventing fluidity, and decreases due to admixing with  $K_2S$ ,  $Fe_2O_3$ ,  $NaOH$ , stearic acid, rosolic acid and galactose are also appreciable.

Lambris<sup>33)</sup> reported an decrease of the tar yield due to the addition of boric acid, and Schauster<sup>34)</sup> also found that a decrease of tar occurred when a lignin was carbonized in the addition of iron oxide. Lambris<sup>35)</sup> described, further, that the effect should be related to OH group in the coal substance, owing to the fact that with the higher oxygen content of coal, the larger was the increase of coke.

Pfeiffer described respecting the acceleration of the blowing process of bitumen how some of the metallic compounds (oxides, sulphates and soaps from manganase, iron, copper, cobalt, etc.), though not increasing the rate of oxidation, shortened the blowing time by reacting with bitumen, resulting in increased hardness and penetration index. With

TABLE 7. Plastic properties of Yubari coal mixed with various substances.

Substances added	Weight of addition %	Softening temp. °C	Fusion temp. °C	Maximum fluidity point		Resolidification temp. °C	Plastic range °C
				temp. °C	fluidity Div/Min		
Fe <sub>2</sub> O <sub>3</sub>	—	373	411	430	17,000	459	48
"	5	377	423	438	1,670	451	28
"	7	382	421	435	188	441	20
"	10	388	427	432	90	437	10
S	2	388	421	434	674	451	30
"	5	418	—	435	17	—	—
K <sub>2</sub> S	5	392	421	432	483	445	24
NaO	5	385	413	432	11,975	454	41
ZnO	5	380	412	432	6,050	454	42
Na <sub>2</sub> CO <sub>3</sub>	5	385	414	435	4,280	452	38
"	10	385	419	435	1,190	455	36
CaCO <sub>3</sub>	10	385	414	432	2,840	452	38
Na <sub>2</sub> SO <sub>4</sub>	5	375	409	433	12,750	455	46
NaOH	5	397	422	430	190	436	14
Creatine	5	378	412	432	2,980	450	38
Stearic acid	5	385	417	433	1,910	451	34
Rosolic acid	5	382	414	432	1,970	450	36
Galactose	5	390	417	432	4,330	451	34
Casein	5	378	411	432	7,190	453	42
Natrium	5	378	409	430	36,600	457	48
Naphtylamin	5	378	409	430	36,600	457	48
Diphenylamin	5	375	407	433	28,550	451	44

ferric chloride, for instance, Pfeiffer stated that the shortening of the blowing time was partly due to accelerated oxidation, partly to reaction of the compound with the bitumen.

In the author's results, the relatively large effect of the organic compounds with oxygen-containing groups (creatine, stearic acid, rosolic acid, galactose), as well as that of NaOH, confirms that the condensation is related to the oxygen-containing groups in the coal, as suggested by Lambris.

Fig. 12 shows amounts of the pyridine- and benzene-extracts in Yubari coal mixed with 5% of sulphur and of galactose when it is heated up to 450°C. The admixing of sulphur very much diminishes

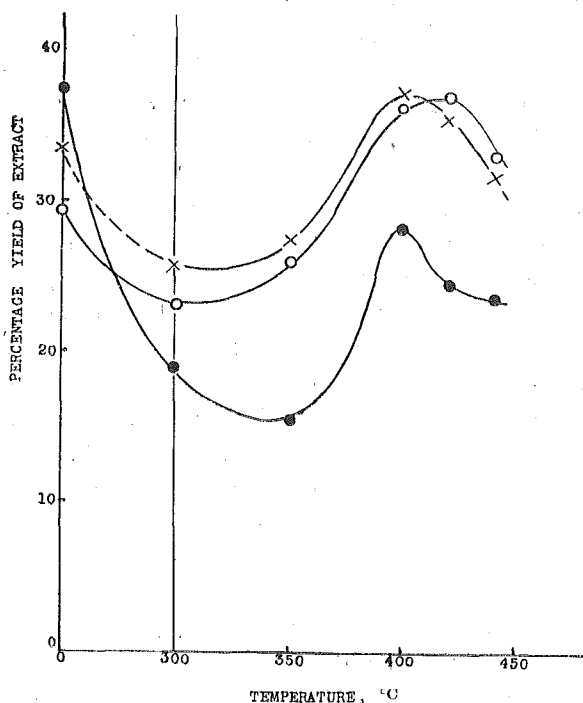


Fig. 12 Pyridine-extract of Yubari coal mixed with 5% of sulphur and of galactose when heated up to different temperatures at 5°C/min.  
 —○— Yubari coal alone.  
 —×— " mixed with 5% of galactose.  
 —●— " " of sulphur.

the amount of pyridine-extract upon the heating. These amounts in the coal mixed with galactose are somewhat lower at temperatures above 400°C than those in the original coal.

In a publication by Lessing<sup>36)</sup> the addition of sulphur is stated to have decreased the tar yield, and in another paper<sup>35)</sup> sulphur lowered the expansion as well as the expansion pressure of the coking coal. Bunte<sup>37)</sup> also observed that the addition of 1% of boric acid decreased the resistance in the gas-flow method, the same as shown by the addition of coke, treatment with pyridine vapour and preheating in nitrogen, when Upper Silesian Seam Coal was tested by the gas-flow method.

According to these facts, a close relation should exist between the caking power and tar yield in the carbonization; the rate of heating,



oxidation and addition of the substances which similarly have some effect on the caking, affect the tar yield in like manner.

Spooner<sup>38)</sup> reported regarding statistical values of the elementary analysis of coals that 4.2% of hydrogen in the coal was the lower limit among the tar yielding coals, as well as among the caking coals. The swelling was proportionate to the hydrogen content in the coals; an equation, the swelling  $\propto$  (hydrogen-4.2), was drawn up. The last equation derived by him who had to recognize a preventing effect by the oxygen content in the coals, was the swelling  $\propto$  (hydrogen-4.2)/(oxygen)<sup>2</sup>.

In Berkowitz's theory the tar which is the driving force of the swelling power to expand in the pores, may be directly connected with the intumescence of coal; the close relation between the caking and tar yield, therefore, must be explained easily under this theory.

It would, however, be more reasonable that the chemical change in the coal constituents as indicated by the decrease of tar yield, should be considered to be of importance in the matter of the caking power. That the change in the coal constituents occurred in the oxidation and carbonization as well as in the coalification, should be recognized to have large effect upon the caking power.

Bawn<sup>32)</sup> stated in his publication that sulphur promoted polymerization, the same as oxygen, and that the action of sulphur would be expected to be similar with that of oxygen because of its two unpaired electrons in the outer shell.

It is, further, known that in the vulcanization of rubber, the formation of cross linking due to sulphur is accelerated by admixing with metal oxides or fatty acids.

These facts must be considered to be evidences respecting to what the effect of admixing with the substances above should be attributed in promoting the condensation of the coal constituents, which occurs in connection with oxygen or sulphur.

Interesting pertinent material is in the report of Takahashi's experiments<sup>39)</sup> in which various organic compounds were carbonized to determine their carbonized residues. In it, the reactivity of unit structure in polymers was reported of essential importance, i.e., the acid radical also was somewhat effective to carbonize, but its effect was promoted by the presence of hydroxyl group to generate the esterification between both radicals; the amount of carbonized residue was affected by the number of active points formed by dehydration. However, the most important factor, of course, was the amount of

aromatic structure. Hence it appears that a number of the oxygen-containing groups, especially of the hydroxyl group, in the coal influences the coke yield among the coals in which the same number of the aromatic structures and of its side chain exist. Some discussion relating to this point will be offered later.

### 3. *Character of the condensation.*

In the discussion up to the present point, the words "condensation," "polymerization" and "cross linking," have been used ambiguously because of their direct descriptive employment in the original papers. The character of the reaction is defined here.

As indicated in Bawn's description, the character of the reaction is considered to be a three dimensional cross linking, which must occur due to the deoxygenation, especially as  $H_2O$ , among the coal molecules with the oxygen-containing outer group, especially hydroxyl group. Here arises a problem of whether or not the groups consist in the coal molecules and are formed by the oxidation.

The presence of oxygen-containing outer groups in low rank bituminous coal is evident because a large amount of the oxygen is removed below  $300^{\circ}C$  in Kakuta coal, Fig. 9; water is considerably expelled from the coal at temperatures below  $300^{\circ}C$ , Fig. 5. It is well known that the oxygen in aromatic nucleus is hardly removed in such a low temperature range.

On the other hand, it is, in general, well known that the aromatics with side chain are easily oxidized to create hydroxyl and carboxyl-groups in their side chain; also the aromatics are more easily oxidized in a mixture of aromatics and naphthenes.

Some further evidence relating to this cross linking theory has been given by Riley's X-ray study<sup>(10)</sup>. It was his finding that the c-axis dimension lengthened appreciably in the plastic state of the caking coal to develop piles of graphitic molecules, but in the low rank non-caking coal, the lengthening of the axis did not appear to develop a three-dimensional cross linking structure. Hence it appears that the development of the plastic state must be affected by the degree of the development of cross linking in the lower temperature range of carbonization.

It was reported by Smith<sup>(11)</sup> who carried out on X-ray study and gas absorption study on carbons from various organic compounds, that the carbon made from the oxygen-poor ones had the turbostratic struc-

ture developed along the c-axis, but carbon from the oxygen-rich ones with large surface area, possessed a high degree of porosity and of the three-dimensional cross linking.

#### Role of the dispersed humin on the plastic state.

It was stated above that the increase of the dispersed humin, above 350°C, as indicated by the pyridine-extract, might be related to the developing of the plastic state, because it appeared in the caking coal, but did not appear in the non-caking coal so oxygen rich as Bibai coal. Further, the increase lowered with the extent to which the coal was oxidized.

Amounts of the pyridine- and benzene-extract in the heated coals, used in table 8, are noted in table 9, and Fig. 13. These experiments were carried on in order to confirm the results on Yubari and Bibai coal, illustrated before.

TABLE 8 Proximate analysis of sample coals.

Coal Name	Moist. %	Ash %	V. M. %	F. C. %	Fluidity Div/Min.
Imported American Coal	1.01	8.31	21.66	69.02	43
Mayaji Coal	1.77	5.66	42.80	49.77	20,000
Ashibetsu Coal	2.17	5.03	43.31	49.49	3,800
Kakuta Coal	5.91	12.39	38.44	42.26	—

In the results, the increase of dispersed humin which accompanied the heating is largest in the low volatile coking coal, whose oxygen content is lowest among the coals tested, and it hardly appears in Kakuta coal being non-caking, the same as in Bibai coal.

Table 10 records the amounts of pyridine- and benzene-extract at the temperatures at which the fluidity is maximum. These values are not necessarily proportional to the maximum fluidity of the coals. If the existence of a close relation between the caking and the dispersed humin in the plastic state, be borne in mind, these results are not considered to be so improbable, because the pyridine-extract in the coals heated by a Soxhlet apparatus after they had cooled, does not agree with the real dispersed humin at that temperature.

TABLE 9 Yields of benzene- and pyridine-extract in various coals heated up to different temperatures at the rate of 2°C/min.

Coal Name	Temp.	Benzene-extract	Pyridine-extract	Dispersed humin
Mayaji Coal	—	3.6	27.2	23.6
"	300	2.9	26.2	23.3
"	325	5.2	25.1	19.9
"	350	9.1	29.2	20.1
"	375	10.2	36.6	26.4
"	400	13.5	35.8	22.3
"	425	14.7	32.0	17.3
"	450	13.8	17.6	4.9
Ashibetsu Coal	—	5.1	27.0	21.9
"	300	4.2	24.9	20.7
"	325	3.6	23.5	19.9
"	350	4.4	25.9	21.5
"	375	3.9	28.6	24.7
"	400	3.6	31.8	28.2
"	425	5.0	26.4	21.4
"	450	5.2	8.5	3.3
Kakuta Coal	—	7.0	15.4	8.4
"	300	6.9	12.6	5.7
"	325	4.5	13.2	8.7
"	350	5.3	15.2	9.9
"	375	6.7	15.4	8.7
"	400	8.2	15.7	7.5
"	425	10.8	13.8	3.0
"	450	5.6	6.5	0.9
Imported American Coal	—	4.5	4.9	0.4
"	300	2.8	3.8	1.0
"	325	4.4	9.1	4.7
"	350	6.3	17.9	11.6
"	375	6.3	16.2	9.9
"	400	5.2	17.6	12.9
"	425	5.9	26.2	20.3
"	450	6.7	25.2	18.5

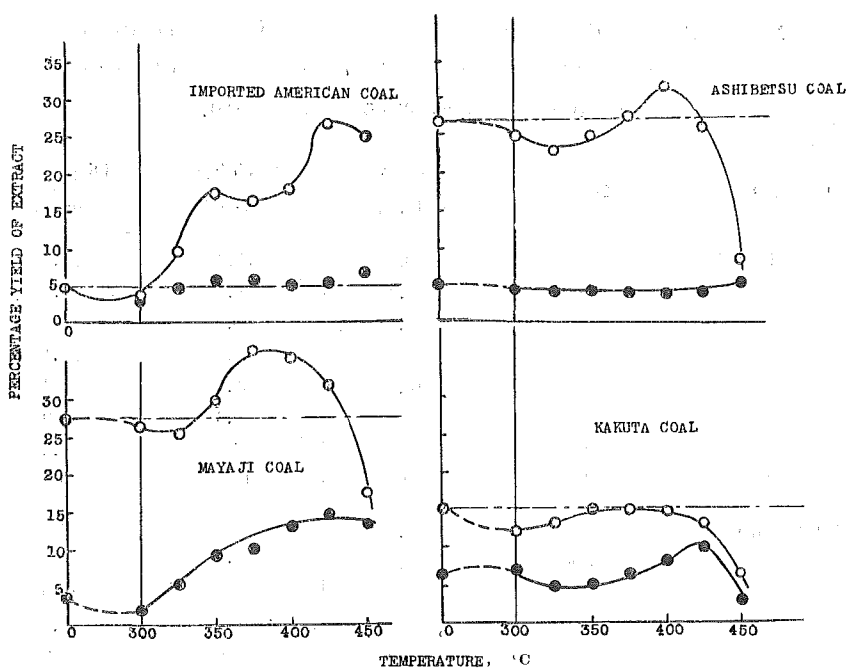


Fig. 13 Amounts of pyridine-extract of various coals heated up to different temperatures.

TABLE 10 Yields of benzene- and pyridine-extract in various coals heated up to the temperatures of maximum fluidity.

Coal Name	Fluidity Div/Min.	Benzene- extract %	Pyridine- extract %	Rate of heating °C/Min.
Yubari Coal	85,000	{ 10.4 8.6 6.0	32.8 33.0 35.1	2* 5 10
Mayaji Coal	22,000	10.2	36.6	2*
Ashibetsu Coal	3,800	{ 3.6 3.2 3.2	31.8 37.7 41.0	2* 5 10
Akabira Coal	140	{ 3.8 3.4	33.5 38.9	5 10
Imported American Coal	45	{ 5.6 4.1 2.7	26.2 14.8 15.9	2* 5 10
Kakuta Coal	—	8.4	15.7	2*

\* The values at 2°C/min. indicate the maximum yields on the curves in Fig. 13.

It has been reported that there is never any essential distinction between characters of the extract in such a solvent with high extracting power as pyridine, and of the extracted residue; the difference whether the constituents are able to be extracted or not, depends upon the size of their molecules. There is a question whether this idea could apply to all kinds of coal, or not.

In the previous paper<sup>1)</sup> the idea was developed that the constituents in a coal with such high fluidity as that from Yubari, should consist of molecules changing continuously in their sizes.

It is, therefore, inferred that the humin actually dispersed during the plastic state may be more than that expected from the amount of pyridine-extract in the coal.

Additionally, consideration should be given to differences in qualities of the dispersed humins, as well as of the solid residuals in the plastic state, among the coals.

Fig. 14 gives amounts of the pyridine-extract comprised in carbon content of the coals. In it, the maximum value of the extract exists near the point of 87% carbon.

On the higher carbon side from the point, the decrease with the carbon content must be attributed to the development of aromatic condensation in the coal constituents to build up the carbon structure, as exhibited by the zero value in anthracite or graphite.

On the other side, however, the decrease following the lowering of carbon content will not be so easily explained. The oxygen in the coals may be recognized to be responsible for it; the difference in oxygen content represents apparently the largest difference among the coals. Consider the large molecular size formed by the oxygen ether link and the strong intermolecular force due to the hydrogen bridge, etc. Certain changes in shape and size of the molecules in the coals may occur in the coalification in the lower carbon side.

At any rate, where the amount of extract is greatest, the fluidity also is almost at its maximum. On each side, therefore, it may be possible that the fluidity increases with the increasing amount of the extract. Hence it appears that as a factor related to the caking power, the dispersible humin originally existing in the coal, as indicated by the extract, should be taken into consideration.

The role of the dispersing humin originally existing in coal in the caking is exhibited in table 11; the fluidity of Yubari coal which was extracted with pyridine, decreases considerably with the time of

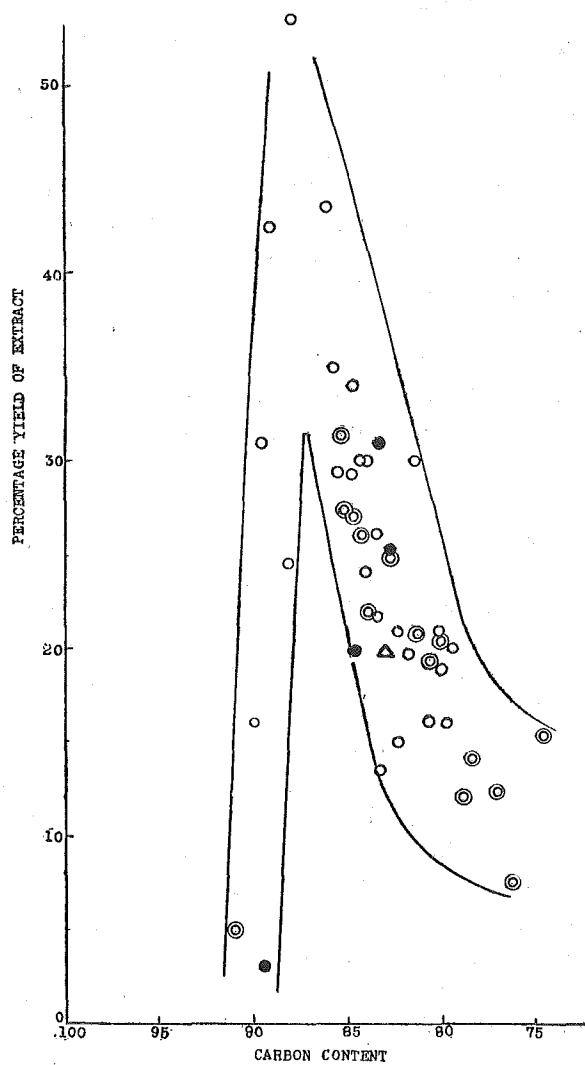


Fig. 14 Yields of pyridine-extract of various coals comprised in their carbon contents.

- Result obtained by Shimmura<sup>21</sup>).
- Result obtained by Bunte (Fuel, 11, 400 (1932)).
- ⊙ Result obtained by the author.

extraction. On the other hand, the fluidity of the coal extracted with benzene does not so appreciably decrease, the same as that of the coal extracted with water. It would be presumed from what most of the dispersing humin remains until the plastic state is reached to develop the fluidity, in spite of some conversions in it by the thermal action.

TABLE 11. Changes of the fluidity of various coals extracted with different solvents for various hours.

Sample Coal	Solvent	Hours of Extraction	Yield of Extract %	Maximum Fluidity Div/Min.
Yubari Coal (1)	—	—	—	46,000
	benzene	8	not measured	21,000
	"	"	"	30,000
	"	14	"	35,000
	water	5	—	31,600
	"	8	—	33,400
	"	14	—	25,000
	pyridine	7	7.8	540
	"	20	9.8	310
Yubari Coal (2)	—	—	—	90,000
	benzene	5	4.2	41,000
	"	9	4.3	38,000
	alcohol	5	1.2	71,000
	"	14	4.0	60,000
Mayaji Coal	—	—	—	24,000
	benzene	5	2.1	3,800
	"	8	2.7	3,300
	"	14	2.9	2,500
	water	5	—	3,400
	"	10	—	5,000
	"	15	—	3,500
Imported American Coal (S)	—	—	—	720
	benzene	5	1.3	440
	"	6	1.3	310
	"	8	1.4	320



### Difference between coalification and carbonization.

The decrease of oxygen content in the coalification which proceeds from the non-caking, low rank bituminous coal to the caking one with high volatile-matter, should be caused by another deoxygenating reaction which is not accompanied by such condensation as in the carbonization.

Krevelen<sup>42)</sup> has reported that the carbonization process is not identical with the coalification one, on the graphical statistical method. Fig. 15 gives results obtained by the elementary analyses as a whole coal differing from those of vitrain by Krevelen. The course, from the low rank bituminous coal to the caking coal with high volatile-matter, is very different from the carbonization process in which a strong tendency of dehydration may be expressed; the course is rather directed along the decarboxylation line. This fact may suggest that the deoxygenation as decarboxylation alone occurred on the coal constituents in this process.

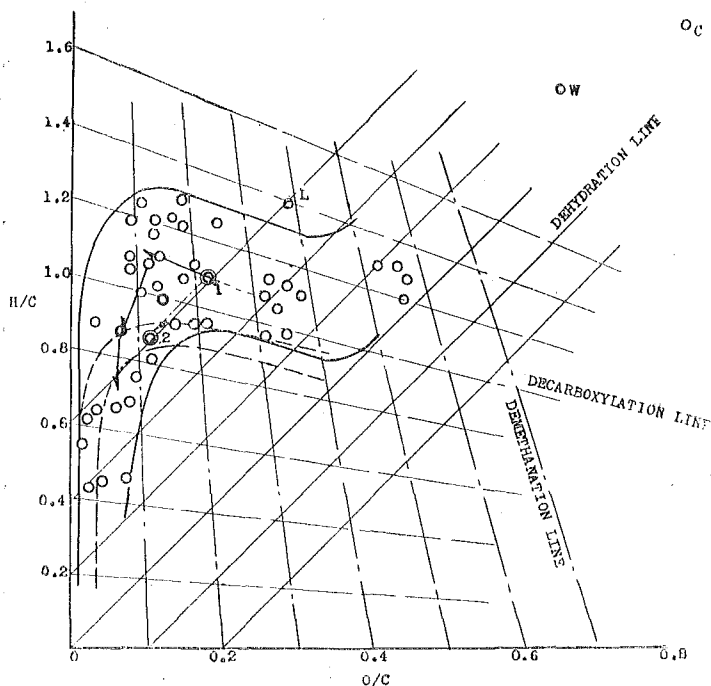


Fig. 15 H/C and O/C of various coals.

L; Lignin. C; Cellulose. W; Wood.  
 ○<sub>1</sub> Kakuta Coal. ⊙<sub>2</sub> Kakuta Coal heated up to 300°C.

It must, anyhow, be true that the deoxygenating reaction in coalification should be almost unaccompanied by the condensation.

The oxygen, therefore, must be removed at least as  $\text{CO}_2$  and  $\text{CO}$  not to disengage the hydrogen from the coal in order that no active free radical be formed. It is known that the caking power of a coal is improved, when it is heated up to about  $250^\circ$  to  $300^\circ\text{C}$  in an aqueous solution of alkali under pressure, and Krevelen has stated that the carbonization of coal under high pressure-water is nearly like the coalification. Surely it is more difficult to drive off  $\text{H}_2\text{O}$  from the coal under a high pressure water. An action of alkali in the solution would have to be taken into consideration, i. e., when natrium benzoic acid is heated, benzene is produced, but, in case of calcium salt such a condensed product, as benzophenon, is formed.

In that case, however, the concentration of alkali solution reacts so delicately upon the coal that, when it is too high to improve the caking power, the coal is rather oxidized to lower the caking power. These point are of interest relative to the fact that there are locally sudden changes of the caking power in the same coal seam.

There is a report published by Krevelen<sup>(3)</sup> in which amounts of the carbons in the hydrocarbons composing the coal were calculated in relation to the coalification as well as to the carbonization. According to him, the aromatic condensation does not so appreciably develop during the coalification from the low rank bituminous coal to the caking coal with high volatile-matter. This fact will be easily expected from the lack of difference in the volatile-matter between them, because of the vital factor of aromatic structure as related to the coke yield. On the other hand, an increase in the coke yield due to the presence of oxygen was described above. Hence there are two factors to increase the carbonized residue, viz., 1) one is the extent to which aromatic structure developed, and 2) the other is the oxygen related to active free radicals formed by the thermal action in the carbonization process. The action of the latter has not been regarded as so powerful as that of the former. Hence it may appear that the presence of same volatile matter in both the coals elucidates why the large difference in the latter would be canceled by the slight difference of the former in the two coals. The change in the coal constituents, therefore, during this coalification, would occur chiefly in the portion other than the aromatic nuclear; it is related to the deoxygenation not to abstract hydrogen in the portion other than the aromatic nuclear.

In the carbonization, furthermore, the chemical change in the coal with high volatile-matter, up to about 300°C, is supposed to be of the nature of dehydration to cause the condensation which differs from the aromatic condensation; the reaction must represent a cross linking among the coal molecules. Above about 350°C, it seems probable that, while mild thermal decomposition in the coal constituents occurs with the evolving of gases, the condensation may yet be rather active, because the deoxygenation also occurs appreciably in that temperature range. In the plastic state, the thermal decomposition of the coal substance is of the most violence to develop the aromatic condensation with formation of so small molecules as to be liquid at this temperature. Besides that, the condensation due to the deoxygenation in the side chain would occur appreciably, especially in the coal having high oxygen content.

### Summary

The consideration respecting why the plastic state does not develop in the low rank bituminous coal, is the principal topic of this paper. According to how the plastic properties are affected by the rate of heating, the behaviour of coal constituents in the heating up to the plastic state, was examined by the pyridine- and benzene-extraction of Yubari coal.

As to the results, a condensation in the coal constituents was recognized to be very active in the temperatures up to 300°C. In as much as  $H_2O$  is only one product in this range, it would be concluded that the condensation should represent the reaction occurring among the coal molecules with oxygen-containing outer group, due to dehydration.

In non-caking Bibai coal which contains more oxygen than Yubari coal, there was not any appreciable amount of increase in the pyridine-extract at temperatures above 350°C, which occurred considerably in the case of Yubari coal. This difference between the two kinds of coal would be attributed to the large development of condensation in Bibai coal, because of its high oxygen content; this fact might be related to the undevelopment of plastic state.

The fluidity of the oxidized coals as well as of them after deoxygenation, was determined by a Gieseler plastometer. In the deoxydized coals, the fluidity of them was lower than that in the oxygenated ones,

in spite of their lower oxygen contents; no relation was observed between the oxygen content and the fluidity.

On the other hand, most of the increased oxygen due to the oxidation was disengaged from the coal by the heating up to the plastic state. Hence it would be concluded that the change of coal constituents as related to the decrease of the fluidity should be due to the deoxygenating process; the change would be attributed to the condensation brought about by the deoxygenation, the same as was stated regarding the oxygen-rich coal.

The hypothesis is confirmed by the facts as follows:

- 1) The increased amount of the pyridine-extract found at temperatures above 350°C in the caking coal, decreased with the extent to which the coal had oxidized; the amounts found in coal so oxidized as to be almost non-caking, were nearly similar with those in noncaking Bibai coal. These facts might be due to the condensation which occurred by the deoxygenation of the increased oxygen in the carbonization of the oxidized coal.

- 2) It is well known that some polymers more easily polymerize in the presence of air than in its absence, for example, polymerization of methyl acrylate at 100°C. When bitumen is oxidized at 100°C and higher, high molecular constituents are dehydrogenated, water being formed, after which the dehydrogenated aromatic remnants condense to large molecules.

- 3) The decreased yield of tar was observed in the coals, which had been oxidized or mixed with various substances. A decrease of fluidity was also caused in the coals. Hence it appeared that a close relation exist between the tar yield and the caking power.

- 4) It is known that sulphur promotes polymerization, the same as is done by oxygen and that it decreases considerably the caking power. Further, in the vulcanization of rubber, the formation of cross linking due to sulphur is accelerated by the admixing with metal oxides or fatty acids.

According to the results obtained from the X-ray studies by Riley or Smith, the character of the condensation was supposed to be a three-dimensional cross linking, differing from the aromatic ring condensation, to develop a turbostratic graphitic structure along the c-axis.

In the coalification process from the low rank bituminous coal to the highly volatile caking coal, the oxygen content, being considered to be the item of largest difference between the two sorts of coal, should

decrease in order not to accompany with such condensation as to be observed in the carbonization. Some considerations respecting that point have been offered.

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