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# Contribution to the Problem of the Caking of Bituminous Coal

Masao KUGO

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### 1. Introduction.

Production of coke of a quality and with characteristics best suited for blast-furnace purposes, and manufactured entirely from Japanese caking coal alone, is a problem which presents acknowledged difficulties.

Only a limited portion of Kyushu caking coal is, by itself, suitable at the present time for producing a good coke which is sufficiently strong to meet the specifications of blast-furnace practice.

Before the war, North Chinese coking coal was imported for the purpose of blending. The requirements of the blast-furnaces in Hokkaido were served by blending imported coal and semi-coke with Hokkaido coal. After the conclusion of the war it became extremely desirable and an economic necessity for Japan to develop technical means for producing suitable coke from her own natural resources thereby eliminating the necessity of importing coal at prohibitive costs, considering the volume required to supply the demand for iron production year by year.

The Japan Iron and Steel Company by its method of testing\* produces with Hokkaido coal a coke which has an indicated "drum index" strength of 75. This is considerably lower than the drum index of 92 which is registered by coke produced from imported coal. This difference is due to excessive development of

\* 10 kilos of an average sample of coke above 50 m.m. is subjected to the action of the drum of which the length and diameter is 1,500 m.m. The drum revolves at 15 r. p. m. and the test is carried out for two minutes. In the side of the drum there are riveted six pieces of plate steel which protrude 250 m.m. into the drum. The coke after the drum test has been carried out is divided into the fractions; above 50, 38, 15 and 6 m.m. The drum index is indicated by the fraction above 15 m.m.

columnar structure of the coke from Hokkaido coal, resulting in the production of "fingery" coke.

Several Investigators up to the present time have applied all available scientific data on the subject of coal carbonization to the problem of producing the coke best suited for blast-furnace use from Japanese coal. Various types of problems, however, seem to remain unsolved as yet especially in connection with Hokkaido coal.

The present investigation, therefore, would be a milestone along the road in an effort to arrive at the upper limits of quality of the coke produced from Hokkaido coal by means of through study related to characteristics of the caking properties of Hokkaido coal, and this paper is one of these efforts to be further continued.

In Hokkaido, caking coal is mined almost entirely from the low coal bearing group in Ishikari coal field and a little is obtained from the Kayanuma coal field. In view of quantity and quality, Yubari coal is recognized as a representative Hokkaido caking coal. Most of the experiments in this investigation, therefore, have been carried out with Yubari coal.

## 2. Benzene-Pressure Extraction

Of the many methods of studying the caking properties or caking constituents of coal, solvent action is one of greatest interest. To many investigators solvent action has appeared of value. An indication of the interest displayed for this phase of coal research can be obtained from the large number of papers which have been published embodying the results obtained from extraction of coal from almost every deposit of significance.

The work of DeMarsilly, in generally, is recognized as the first to extract coal with solvents referring to the caking properties and the later works have been essentially summarized by Kiebler<sup>1)</sup>.

In this research the benzene-pressure extraction was carried out in order to confirm the theory<sup>2)</sup> that the caking properties are affected not only by the extract but also the extracted residue.

**Table I**  
Proximate Analysis and Result from Extraction

Coal		Proximate Analysis				Extraction	
No.	Bed	Moisture	Ash	Volatile Matter	Fixed Carbon	Percent of Extract	Caking Properties of Extracted Residue
1	Yubari	1.56	6.49	45.23	46.75	12.6	good
2	Kayanuma	0.92	14.41	27.89	56.99	9.7	non
3	Bibai	2.94	5.22	47.11	44.74	5.1	non

Table I shows the proximate analysis of the coals tested.

The test procedure was as follows :

A bag made of glass cloth protected by 325 mesh-sieve-netting was charged with 50 grams of coal, passing through 65 mesh, and then suspended from a lid of a 500 c.c. vertical autoclave. The extraction was carried out repeatedly, in the usual manner, at 250°C for 3 hours with 350 c.c. of benzene in the autoclave.

After both the extract and residue had been dried up in vacuum, yield of the extract was calculated in percent.

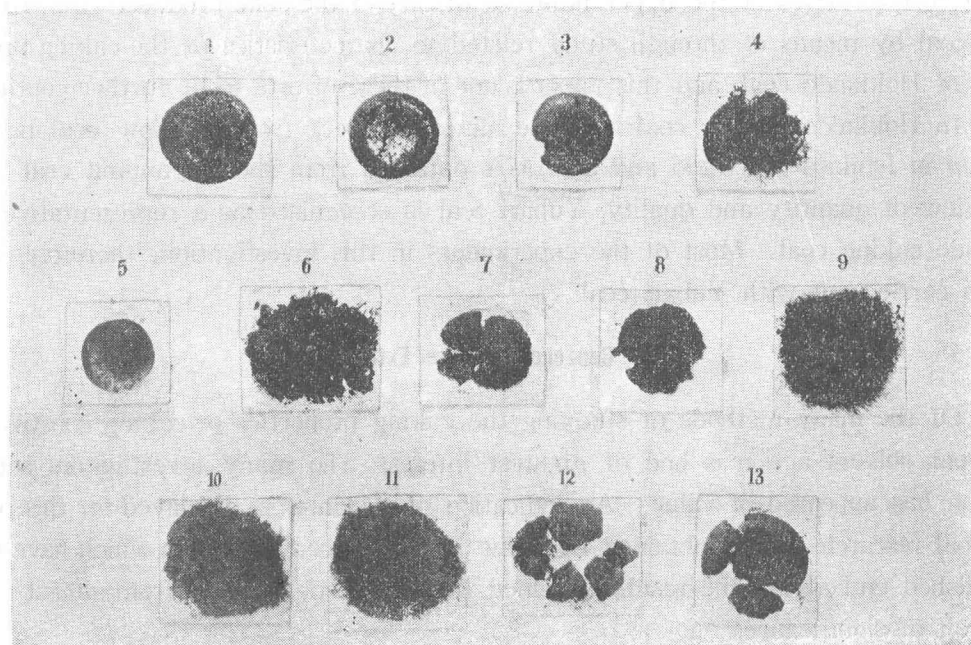


Fig. I. Coke button obtained from following coals, extracted residues, and residues remixed with extract.

1. Coal I.
2. Residue of coal I extracted with pressure-benzene at 250°C for 15 hours.
3. Residue of residue 2) extracted at 220°C for 9 hours.
4. Residue of coal I extracted with tetraline at 25°C for 20 hours after extraction with benzene at 250°C 15 hours.
5. Coal 2.
6. Residue of coal 2 extracted with benzene at 25°C for 15 hours.
7. Residue 6) mixed with 10% of extract of coal 3.
8. Residue 6) mixed with 10% of extract of coal 2.
9. Coal 2 oxidized with air at 170°C for 3 hours.
10. Coal 3.
11. Mixture made up of residue of coal 3 extracted with benzene at 25°C for 9 hours and 5% of extract of coal 2.
12. Mixture made up of extracted residue of coal 3 heated with hydrogen of initial pressure of 30 atm. at 25°C for 3 hours and 5% of extract of coal 3.
13. Mixture made up of extracted residue of coal 3, after treated as 12), heated with hydrogen of initial pressure of 100 atm. at 25°C for 3 hours and 5% of extract of coal 3.

Determination of the caking properties of samples was arrived at by observing the coke button obtained in the crucible which was charged with 2 grams of sample and heated in a vertical electric furnace to 500°C at the rate of 5°C per minute and then maintained at 500°C for 30 minutes.

The remixing the residue with the extract was carried out by resolving them with benzene in a crucible and then distilling away benzene in vacuum.

The result of the extraction is denoted in Table I. Coal I retains not only the caking power but somewhat the swelling characteristics as shown in Fig. 1, in spite of the perfect destruction of the caking power of coal 2. Therefore, this extracted residue of coal I again having been extracted for 9 hours at 280°C, resulted in a yield of the extract of 2.4 percent afresh; but the residue did not yet lose its caking power (No. 3 in Fig 1.). This fact seems to be contrary to the works of Fischer<sup>3)</sup> and Bone<sup>4)</sup>, who found that the residue extracted with pressure-benzene lost the caking power and the caking power of coal completely imputed to the extracted part. It is, therefore, very interesting that coal 1 shows the characteristic differed from the coal tested by them.

The residue of coal 1 extracted with benzene at 250°C for 15 hours was further extracted with tetraline for 20 hours at the same temperature, 250°C, and the total yield of the extract was 16.7 percent

The caking power of the residue is almost lost as No. 4 in Fig. 1. The decrease of the caking properties of coal 1 by the extraction with pressure-benzene, here, is found to be very slow and progressive.

Peter and Cremer<sup>5)</sup> also extracted  $\mu$ -coal with benzene in an extractor working on the Soxhlet principle. The data from these runs indicated that the extract obtained with benzene consisted of two parts, one which was very easily and rapidly removed, and the second which was much less soluble. Somewhat similar results were obtained by Illingworth<sup>6)</sup>. The elementary analysis of the pentane soluble and insoluble parts did not indicate differences which would have satisfactorily explained the differences in properties of these materials which range from oil like materials to not readily soluble amorphous solids.

Fischer and Peters<sup>7)</sup> have reported that coals through hydrogenation could be converted to "pseudobitumens" which had properties similar to the bitumens obtained in extraction with benzene.

As Kiebler has described<sup>8)</sup>, therefore, it could be regarded as a conclusion that the extracted material differs chiefly in degree of polymerization rather than in composition.

Other works suggested that only the resinic part of the coal was dissolved and the remaining apparently soluble material was in reality dispersed as colloidal

aggregates.

From the result obtained by this experiment, therefore, a hypothesis would ensue as follows:

On coal 1, the constituents polymerized up to the degree with which the caking properties might concern themselves are contained in a large quantity and a distribution of continuous size of these polymerized units within the relatively wide region of which centre would exist near the limits of the benzene-pressure extraction. On the other hand, on coal 2, as displayed by its less volatile matter, the polymerizing degree of the constituents by the coalification grows up to such extent that the separation of the caking constituents by the extraction may be not so difficult.

In other words, as the constituents so polymerized as relating to the caking power would be distributed in a series of continuous units approaching the limits of the extraction as on coal 1, the constituents could not be completely removed by the extraction with benzene, but the constituents, having altered progressively to smaller and larger units, could be separated more easily, on coal 2.

The characteristics of Hokkaido caking coal can be found on coal 1, as having a high volatile matter content, and coal 2, being almost the same sort of the coal as tested by Fischer and Bone, containing medium volatile matter which produced coke suited for blast-furnace use, but its quantity in Hokkaido is very limited, and its sulphur content is as high as 2 to 3 percent.

The result of remixing the extracted residue of a coal with the extract of another coal is illustrated, No. 7 to 9 and 11 in Fig. 1. The restoration of the caking power by remixing of the separated constituents might be considered as unsatisfactory, in that the coke from the residue from coal 2 mixed up with its own extract is not perfectly similar to that of the original coal. The mixture consisting of the residue from good caking coal 2 and the extract from noncaking coal 3 exhibits a little caking power as No. 7 in Fig. 1, while the other consisting of the residue from noncaking coal 3 and the extract from good caking coal 2 shows completely no caking power as No. 11 in Fig. 1.

In addition to the above, 20 grams of coal 2 having been oxidized for 3 hours at 170°C through air flowing at the rate of 300c.c. per minute by the apparatus shown in Fig. 2, resulted in its caking power being destroyed completely as No. 9 in Fig. 1. The residue of coal 2 which was alone oxidized under the same condition, also could not restore the caking power, after having been mixed with its own extract. After the residue from coal 3 had been heated in a autoclave for 3 hours at 250°C, initial pressure of 30 atm. of hydrogen and then further for 3 hours at the initial pressure of 100 atm., these residues were mixed with its own extract

and carbonized as No. 12 to 13 in Fig. I. Some progressive improvements in the caking power can be found there.

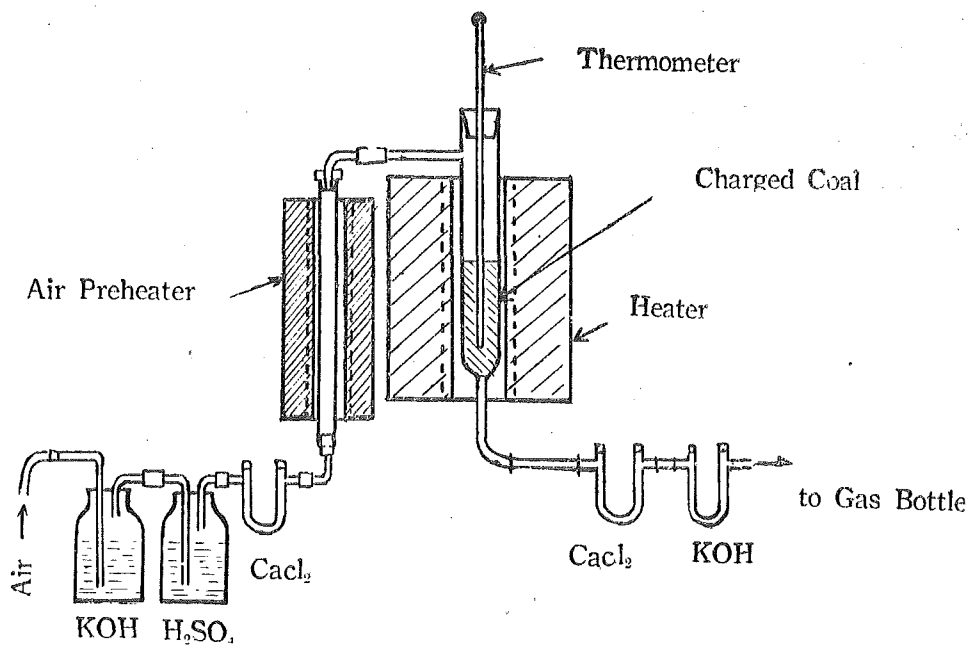


Fig. 2. Oxidation Apparatus

All these phenomena certainly confirm the results found by Drees and others<sup>2)</sup> to suggest the importance of the residue in the region to which the caking properties refer. Even if the residue should not by itself display the caking power, it would have a great influence upon the caking power of coal in respect to the coal as a whole.

### 3. Influences of Heating Rate, Addition of Inorganic and Organic Substances upon Swelling Power of Coal.

The influence of the rate of heating upon the swelling power of coal has long been recognized.<sup>9)</sup> Lambris<sup>10)</sup> discussed in minute detail the crucible tests and swelling tests under an applied load and pointed out that the results obtained by such methods usually were not comparable among themselves and never showed the maximum possible degree of swelling of a coal, because the manner of heating permitted a crust of coke to form around the noncoked portion of the coal sample and prevented its further expansion.

Certainly these tests are so delicate that the values of swelling are not closely duplicated and the results obtained by different apparatus are not comparable to each other, but it can be recognized as true that, in a series of results obtained

by the same apparatus and operator, the values could be comparable to each other and show a general relation among the coals tested.

Warren<sup>11)</sup> has studied the effect on yields of carbonization products at changing rates of heating through the preplastic range and found that the higher the rate of heating, the greater was the yield of coke. According to these facts, he has suggested that with rapid heating the number of small molecules which survived until a high enough temperature was reached for them to escape through mild decomposition and distillation was larger than at slow rates of heating where reaction between the small units has largely converted them to relatively large molecules, which would not distill without active decomposition and consequent conversion in great part to coke and gas<sup>12)</sup>.

The thermal cracking characteristics of coal 1 obtained by Oshima-Fukuda

thermobalance also illustrate some differences between yields of the coke residues heated at the various rates of heating, Fig. 3.

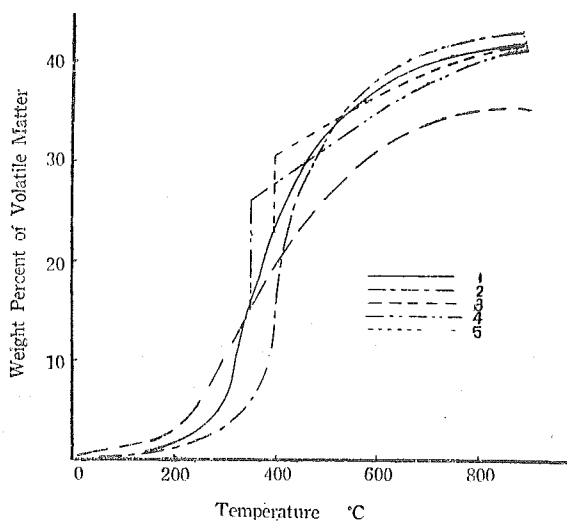


Fig. 3. Thermal Characteristics of Coal I  
 1. 5°C/min 2. 2°C/min 3. 2°C/min  
 4. Maintained at 375°C for 1 hour  
 5. " at 400°C for 1 hour

Here a problem has arisen, which is to determine whether the variation of the swelling value accompanying a change in the rate of heating is responsible for the alteration of the plastic properties being dependent upon the condensation during the preplastic state as pointed out by Warren, or whether the change of the evolving rate of volatile matter during the plastic state becomes a source of variable expansion pressure.

The evolving rates of the volatile matter differ as shown in Fig. 3; the higher the rate of heating, the more rapid the evolving rate that occurs within the temperature region, 370 to 470°C.

In this investigation the determination of the swelling value was carried out by an usual apparatus constituted of two cylinders, a load of piston type set on the charged coal, and a vertical electric heater. The cylinder made of silica was put in the other cylinder made of unglazed pottery and a thermocouple was set in the clearance of them at the height of the coal charge. Two grams of coal 1, passing through 65 mesh, were poured into the inner cylinder and compressed to the volume of 0.7 times of the original one. The load was 100 grams and its movement occ-



ured by the coal swelling was automatically recorded on a rotating drum. The value of swelling was defined as the ratio of the maximum height to the original one in percent.

Table II denotes the results obtained from the two rates of heating and prolonged heating at the three temperatures during the heating period.

As the temperature maintained during the heating period approaches the plastic temperature, the diminishing of the swelling value becomes larger. The difference of the evolving rate during the plastic range at the various maintaining temperature, as in Fig. 3, is so appreciable that the variation of the swelling values may depend on it. In addition, it should suggest the importance of the evolving rate as source of the expansion pressure that the value of the swelling, as the heating rate was elevated to 20°C per minute after having been maintained at 380°C for one hour, is larger than that at the rate of heating unchanged.

Lambris<sup>(3)</sup> investigated the effect of the addition of boric acid and sulphur upon the expansion pressure, softening behavior and yield of distillation products of expanding caking coals and found that the coal was mixed with 0.3 to 0.5 percent of boric acid and heated progressively within the softening stage, the coal no longer showed expansion. He<sup>(4)</sup> also showed that with the addition of boric acid, the higher the oxygen content of the coal, the more was yield of coke, and suggested a hypothesis that the effect of boric acid was related to the hydroxyl groups of coal and formed complexes with them.

It is probable that this reaction related to the hydroxyl groups would correspond with the condensation suggested by Warren and the addition of boric acid would promote the condensation.

The effects of addition of compounds upon the swelling properties of coal I and a high swelling coal (ash 12.06%, volatile matter 27.90%) were observed here. The effects of addition of inorganic compounds are shown in Fig. 4.

Considerable effect was observed from sulphur and iron oxide on both coal. Kalium sulphide, natrium oxide and natrium carbonate have no appreciable effects on the high swelling coal, but somewhat effect coal I.

Table III denotes the data of addition of the organic compounds upon coal I.

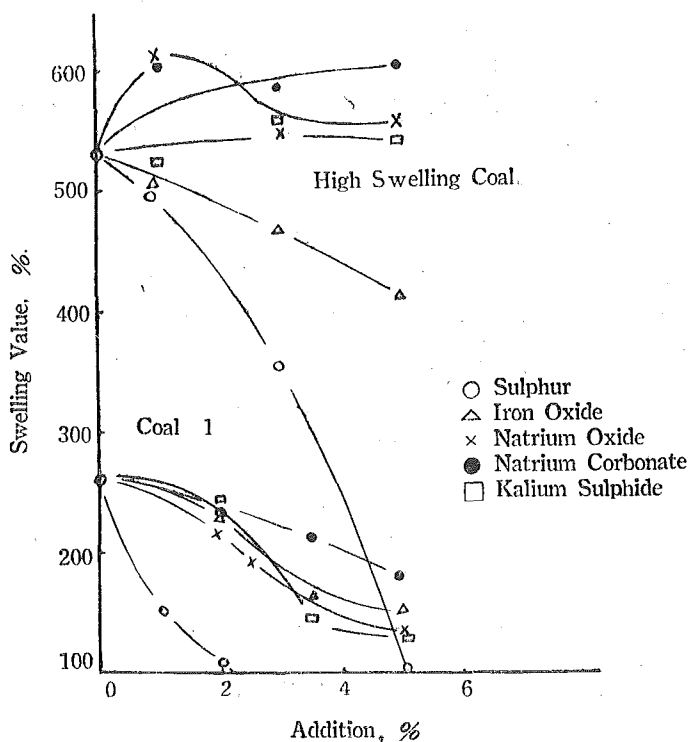
Table II  
Data of Swelling Value

Temperature°C Maintained for 1 hour	Rate of Heating °C/min	Percent of Swelling Rate
—	5	270
—	2	140
350	5	260
380	5	220
380	* 5—20	280
410	5	210

\*Heating rate was raised from 5°C/min to 20°C/min after maintaining at 380°C for one hour.

**Table III**  
Effect of Additin of Organic Compounds upon  
Swelling of Coal

Compound	Percent of Addition	Percent of Swelling	Percent of Difference from Swelling Value Added with Sand
Rosalic Acid	5	230	+ 5
Naphtylamin	5	260	+ 35
Galactose	5	238	+ 13
Diphenylamin	5	206	- 19
Stearic Acid	5	303	- 22
Casein Natrium	5	143	- 63
Creatine	5	110	- 115
Sand	5	225	0



**Fig. 4.** Influence of Addition of Organic Substances upon Coal I, and High Swelling Coal

There are the mild effects of amins and acids, but those of casein natrium and creatine are very severe. No appreciable differences were recognized among the thermal characteristics whether or not these compounds were added in Fig. 5, the influences of addition of them upon the swelling power must be attributed to

the alteration of the plastic properties. As shown by the decreasing swelling values, casein natrium and creatine radically would affect the plastic properties to have promoted the condensation during the preplastic state as indicated by Warren.

Some alterations of the plastic properties through the addition of those compounds, indeed, were observed already by the plastometer method, which will be reported in a later paper.

Although no systematic investigation has been in operation, the chemical construction of the compounds that would promote the condensation of coal substance during the relatively low temperature are very interesting.

#### 4. Plastic Properties Measured by Plastometer

The pioneer work of the plastometer was that of Davis,<sup>15)</sup> who suggested the importance of the plastic state in the investigation of the coal carbonization. Extensive experience<sup>16)</sup> with the plastometer has taken place elsewhere, but in Japan this sort of the coal investigation has not been carried out yet.

Here, the modified Gieseler plastometer<sup>17)</sup> was used for the measurement of the plastic properties.

In the Davis plastometer method the coal charge as a whole is rotated and stirred; the properties measured are the resistance to shear of the partly fused coal adhering to the periphery of the retort. On the other hand, in the Gieseler's principle the coal charge is static at first but is later stirred at a rate proportional to the fluidity developed in the coal. Rotation of the stirring shaft is caused by the application of a constant torque force on the shaft. With increase in fluidity beginning of the heated coal, the rate of rotation of the stirring shaft increases. At the beginning of the solidification of a melted coal mass into semicoke a coal rapidly loses its fluidity and as semicoke formation proceeds this movement falls off rapidly to zero.

The dimensions of this apparatus used here are shown in Fig. 6. The total frictional resistances produced in the rotating parts are corresponding to 8 grams of the load by which the constant torque on the shaft is caused, as illustrated in Fig. 7,

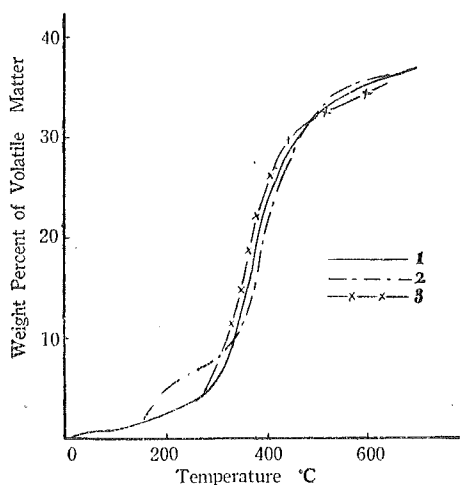


Fig. 5. Thermal Characteristics Added with Inorganic Compounds at 5°C per Minute  
1. Coal 1 alone 2. Added with Sulphur 3. with Kalium Sulphide

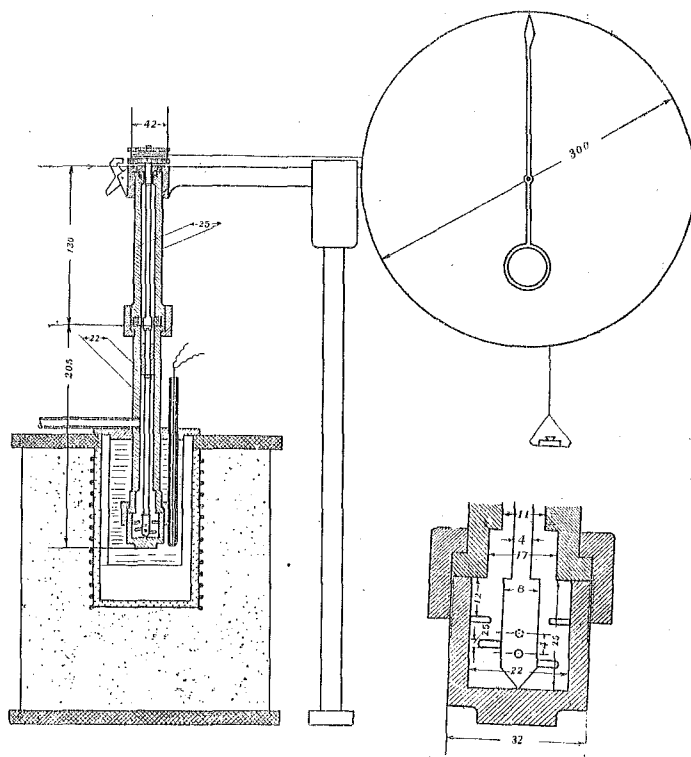


Fig. 6. Plastometer

which contains the fluidity curves measured for tar-pitch added with coke at 100°C and castor oil at the various low temperature by this apparatus. The load on the load pan was 20 grams and the pan was 16 grams in this experiment. Heating

was carried out at rate of 2.5°C per minute in the metal bath of which melting point was 140°C.

The temperature in the centre of the coal charge in the retort was found to be lower by 8°C at 2.5°C per minute than that obtained by the thermometer shown in Fig. 6, which was one at the same level in the bath or the outside wall of the retort. This temperature difference is almost two times that of the one found in Brewer's apparatus.

The test procedure was as follows:

The retort was charged with 4 grams of coal, passing through 35 mesh, and then the charge was compressed for 15 minutes under 10-kilos load, the same as in Brewer's work.<sup>17)</sup> The apparatus was lowered into the bath, pre-

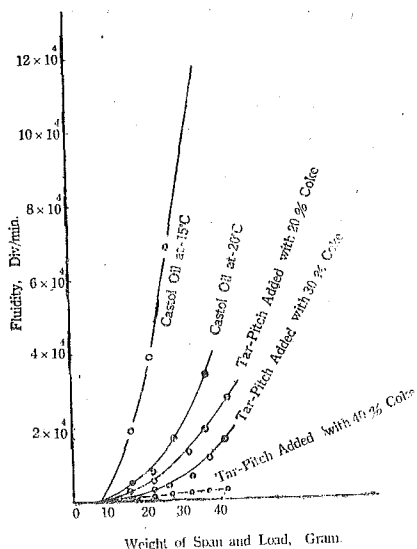


Fig. 7. Fluidity of Castor Oil and Tar-Pitch Added with Coke at Various Loads

heated to 200°C. Introduction of the cold apparatus so reduced the bath temperature that about 15 minutes time was required to bring it to 160°C. After reaching to 160°C, the temperature was maintained 15 minutes and then was raised at rate of 2.5°C per minute. Readings of temperatures scale were made each time and the pointer movement was read on the 1000-scale-division dial.

The reading numbers indicated in table V, therefore, are ten times of those shown by Brewer. From the observed times, temperatures and dial readings the corresponding number of pointer revolutions was calculated in dial division per minute.

The logarithms of these latter values are plotted as ordinates against temperatures in degrees centigrade as abscissa (Fig 8).

Table IV illustrates the analysis of the coals tested.

The results of these coals are shown in table V. In expressing these data, according to the Brewer's method, there are taken: (a) the initial softening temperature corresponding to 1 dial division per minute; (b) the fusion temperature at 50 divisions per minute on the ascending portion of the plastic curve;

(c) the maximum fluidity temperature at the maximum rate of pointer movement; (d) the solidification temperature at 50 divisions per minute on the descending portion of the plastic curve; (e) the temperature of the end of the plastic range taken when the pointer shows no further movement.

Brewer has shown that this arbitrary selection of temperature points (a), (b) and (d) gave values consistent with the corresponding characteristic temperature points established by the Agde-Damm and Davis methods.

The coals of which the maximum fluidity is below 50 divisions per minute in Table V are considered as not being truly caking coal which produce mostly powdered coke, as the definition above indicates. Furthermore, coal 4 to 7 show ext-

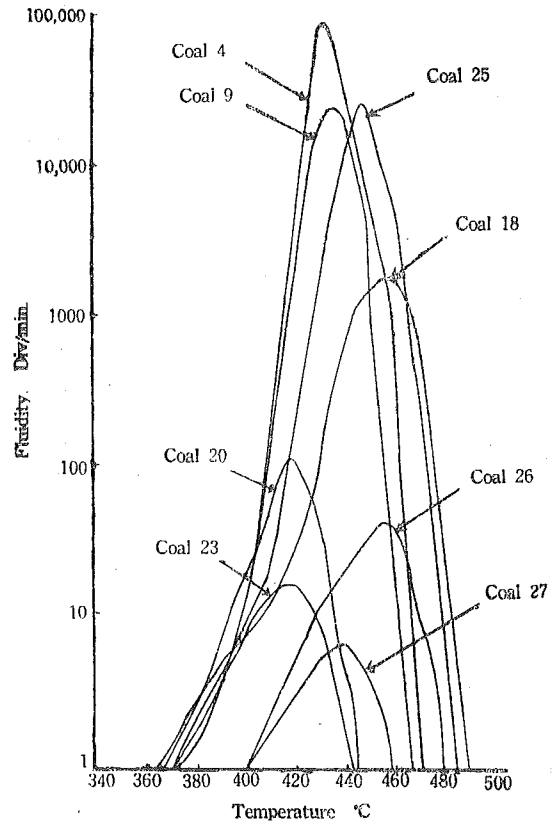


Fig. 8. Plastic Curves of Coals Determined by Plastometer.

Table IV. Analysis of Coal

No.	Coal		Proximate Analysis				Ultimate Analysis (dry, ashless basis)					Drum Index of Coke	
			Mois- ture	Ash	Volatile matter	Fixed carbon	C	H	N	S	O		
4	Ho- kaido	Yubari	1.48	13.56	39.88	45.08	81.91	5.37	3.15	0.36	9.21	75~80	
5		Ohyubari	0.87	8.32	42.07	48.74	82.21	6.33	3.86	0.25	7.35	75~80	
6		Kayanuma	0.74	16.42	33.32	49.52	85.30	6.04	5.16	3.24	0.26	70~75	
7		Ashibetsu (K)	1.32	6.76	38.40	53.52	74.21	5.48	8.50	0.57	11.25		
8		Toyosato	1.36	7.66	39.12	51.86	78.70	6.75	4.87	0.59	9.09		
9		Mayazi	2.10	13.76	39.84	44.30	73.48	6.31	3.46	0.26	16.49		
10		Sunagawa	1.50	8.68	40.89	49.00	82.25	5.74	4.01	0.51	7.49		
11		Utashinai	2.08	12.58	37.14	48.02	78.39	4.82	4.94	0.68	11.17		
12		Kamoi	2.04	10.46	38.04	49.46	84.10	5.51	3.43	0.65	6.31		
13		Moziri	2.00	11.26	47.50	39.24	78.41	6.02	4.17	0.55	10.85		
14		Kamiutashinai	2.12	6.84	41.28	49.76	82.49	5.81	5.07	0.63	6.00		
15		Akabira	2.64	8.60	40.84	47.92	82.77	6.13	4.23	0.83	6.04		
16		Ashibetsu	3.12	5.92	41.08	49.88	76.28	5.18	4.24	0.70	13.60		
17		Kyushu	Miike	0.86	12.08	40.92	46.14	84.06	6.92	4.89	0.21	3.92	9)~ 65~70
18			Shishimachi	0.82	8.90	24.76	65.52	89.54	5.37	3.27	0.60	1.22	
19			Kambayashi	0.74	7.56	24.76	66.94	88.77	5.42	4.30	0.68	0.33	
20	Kaho		2.28	10.52	39.79	47.41	84.27	6.40	4.10	0.53	4.70		
21	Tadakuma		2.12	15.26	37.58	45.04	83.07	5.95	3.86	0.72	6.40		
22	Uruno		2.62	16.12	36.02	45.25	78.20	5.51	2.55	1.03	12.71		
23	Hojo		3.96	16.00	35.64	44.40	76.64	5.14	2.90	0.48	14.84		
24		Imported Coal (P)	1.38	7.68	17.46	73.84	85.65	4.88	1.23	0.87	7.37	90~	
25		" (S)	1.84	6.44	22.38	63.34	87.35	4.42	3.10	0.72	4.42	9)~	
26		" (R)	1.80	6.96	21.94	69.30	89.54	5.64	2.41	0.83	1.58	90~	
27		" (M)	1.22	16.45	24.15	58.18	84.73	4.57	2.67	0.82	7.21		

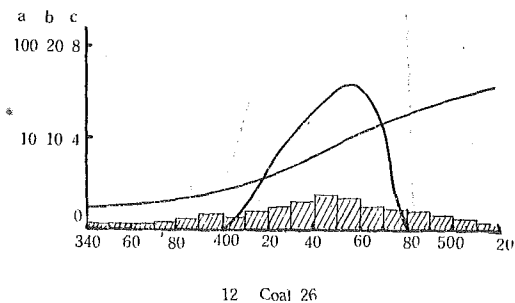
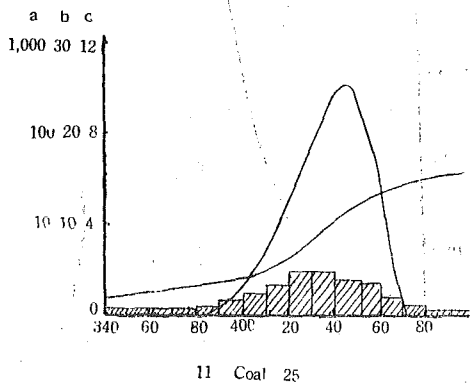
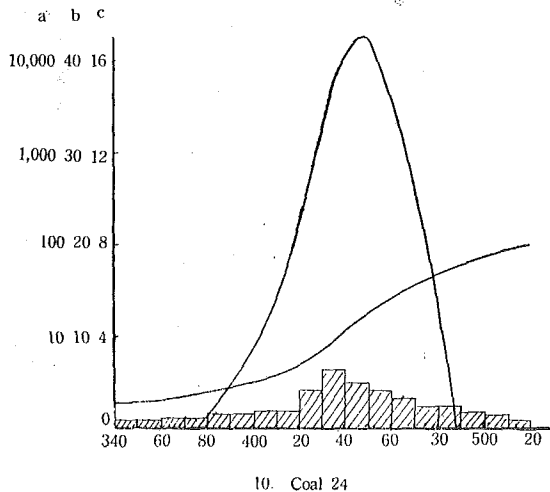
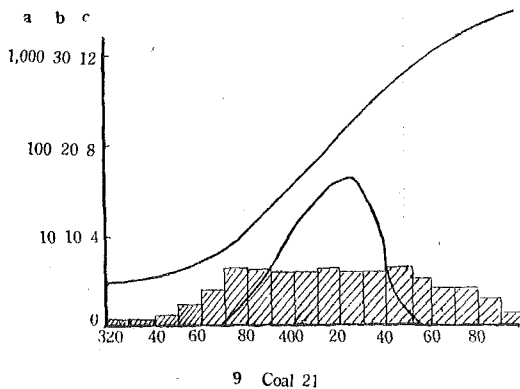
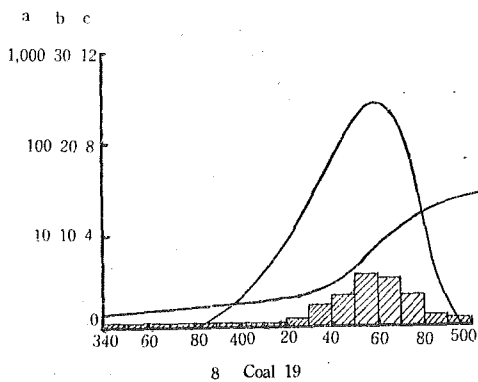
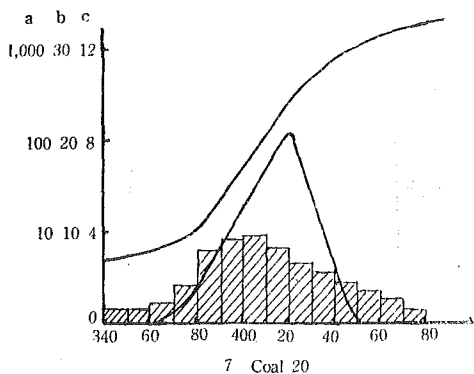
Drum index measured by Japan Iron and Steel Company method

remely high fluidity. On account of this high fluidity referring to its high swelling power and high volatile matter content, the measure was so difficult that the results obtained for these coals are not so exact as those of the coals having middle or less fluidity.

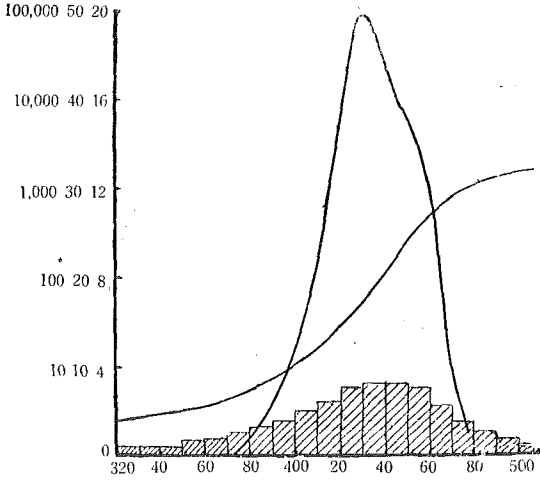
With regard to the temperature of the maximum fluidity, that of high volatile coal is evidently lower than that of medium volatile coal. There are, however, no differences of the maximum fluidity between coal 9 and coal 24; coal 13 and coal 18; coal 16 and coal 26, in spite of the appreciable differences of the temperature of the maximum fluidity, volatile matter and quality of coke from each coal. Therefore, it is difficult to judge the quality of coke and the coal rank of caking coal according only to the maximum fluidity obtained by this method.

Fig 9. Plastic Curves and Thermal Characteristics

- a Fluidity, Div/min.
- b Volatile matter, %.
- c Volatile Matter, % of 10°C Interval.

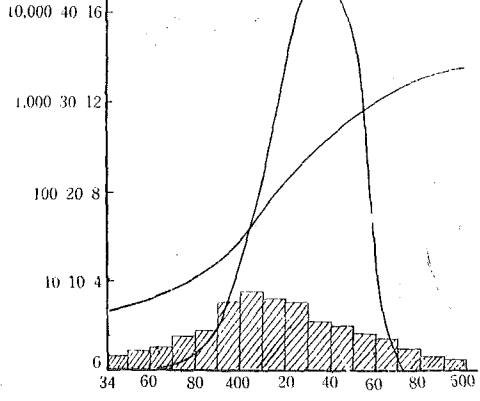


a b c



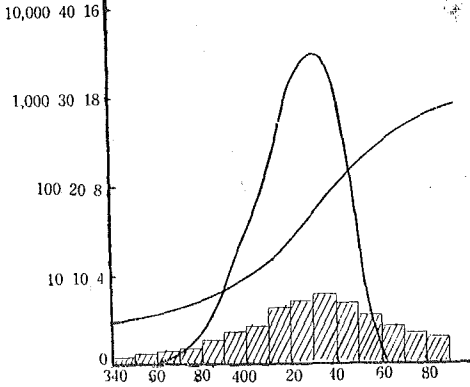
1. Coal 4

a b c



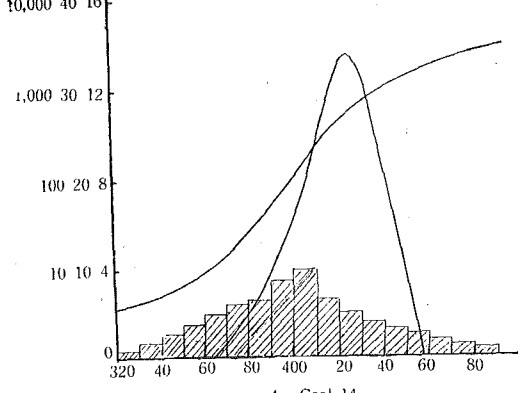
2. Coal 9

a b c



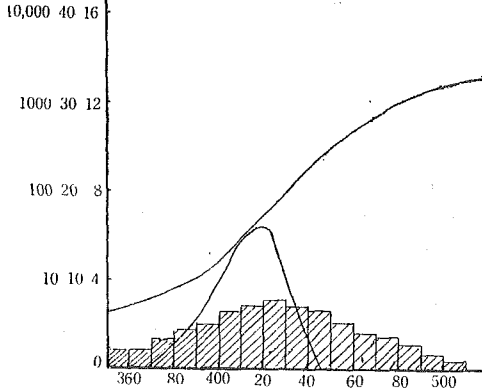
3. Coal 12

a b c



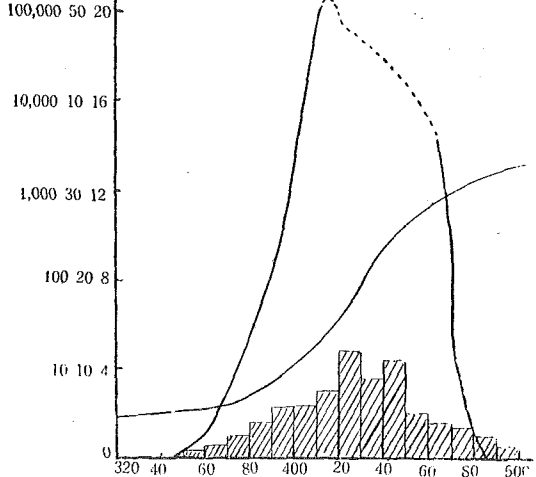
4. Coal 14

a b c



5. Coal 16

a b c



6. Coal 17



Table V. Result of Plastometer Test

Coal No.	Initial Softening Temp. °C	Fusion Temp. °C	Maximum Pointer Movement		Solidification 50 dial divisions	End of Plastic Range °C	Plastic Range 50 dial divisions or more, Pointer movement. °C
			°C	Div/min			
4	358	403	430	90,000	461	472	58
5	360	408	433	100,000~	479	482	71
6	350	408	434	94,000	465	480	57
7	355	397	430	33,000	457	472	60
8	353	407	433	30,800	463	474	56
9	362	435	434	23,000	459	470	52
10	363	412	435	14,000	458	471	46
11	364	409	435	5,400	452	475	43
12	362	407	428	3,800	448	460	41
13	368	412	437	2,270	454	466	42
14	363	404	427	1,700	444	451	40
15	370	410	427	102	434	450	16
16	368		421	43		445	
17	340	385	420	100,000~	472	476	87
18	382	426	457	2,100	472	488	46
19	390	440	458	245	476	492	36
20	360	411	420	122	457	466	46
21	365		425	45		446	
22	378		418	16		448	
23	398		420	3		465	
24	373	417	448	24,000	454	485	27
25	395	427	446	360	453	472	26
26	400		455	48		480	
27	405		439	7		462	

From the plastic curves in Fig. 8, a certain relation might be deduced among the maximum fluidity, the temperature of it and the coal rank; with rising temperature of the maximum fluidity, the maximum fluidity increases till reaching its maximum value and then progressively decreases. In the last stage the temperature of the maximum fluidity might incline to descend with decreasing of the maximum fluidity.

Fig. 9 illustrates the plastic curves and the thermal characteristics of some typical coals among the coals tested.

In Fig. 10 a somewhat linear relation is obtained between the temperature of

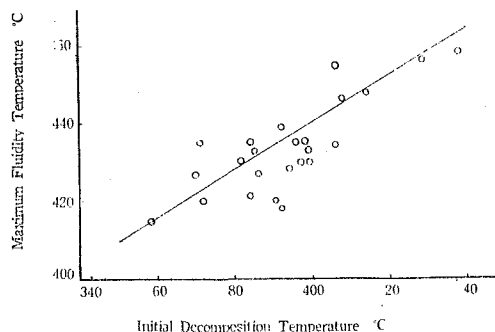


Fig. 10. Relation of Maximum Fluidity Temperature to Initial Decomposition Temperature.

the maximum fluidity and the initial temperature of the rapid decomposition, from the thermal characteristics; the temperature of the maximum fluidity as well as the initial temperature of the rapid decomposition has a parallel relation to the coalification degree.

On the other hand, no relations have been found to exist between the temperature of the maximum fluidity and the temperature range during which the maximum amount is expelled among the intervals of 10°C. There is, however, a certain relation recognized between the maximum fluidity and the amount volatilized

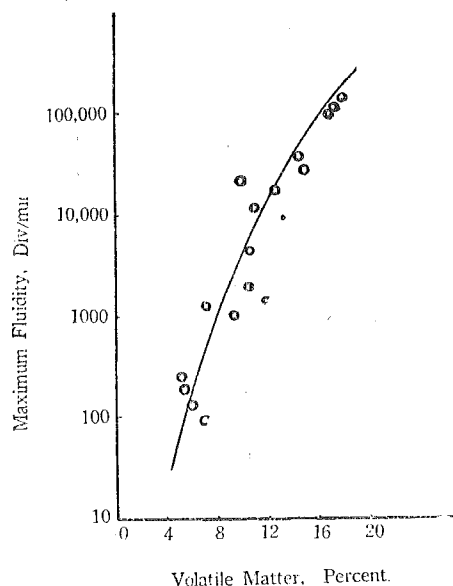


Fig. 11. Relation of Maximum Fluidity to Volatile Matter during Plastic Range.

temperatures up to 425°C, after which a decrease in phenols, bases, and acids occurred, and the cumulative yield of the total extract increased progressively to 450°C.

His paper has shown evidently the fact that a certain portion of the pressure-benzene-insoluble constituents had been converted into the soluble one by the thermal degradation of coal substance at relatively low temperature.

Coal 1, passing through 65 mesh, after having been heated to the various temperatures up to 425°C at rate of 5°C per minute in a vertical silica tube, was extracted

during the plastic range defined as 50 dial divisions or more per minute as in Fig. 11; the higher the former, the greater is the latter.

These facts would suggest a close relation that would lie between the plastic state and the thermal reaction during the preplastic and forepart of the plastic state.

Asbury<sup>18)</sup> divided the material from the benzene-pressure extractions into acidic, basic, and neutral ether-soluble and-insoluble fractions and found that there was a general rise in acidic, basic, phenolic, and neutral ether-soluble material with increasing temp-

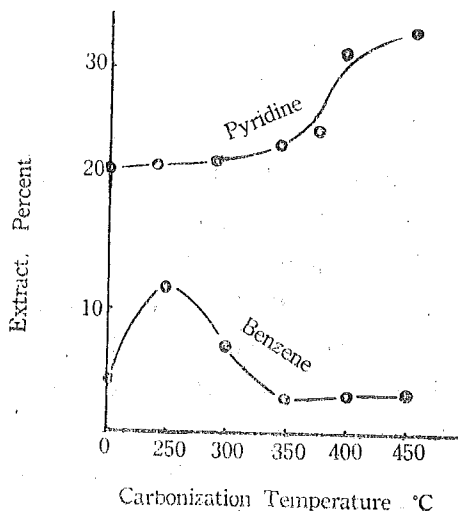


Fig. 12. Extraction of Coal 1 Carbonized, with Pyridine and Benzene.

with benzene and pyridine in the Soxhley apparatus. As in Fig. 12, the extract with pyridine increases from 375°C to suggest the insoluble constituents being considerably converted into the soluble ones by the thermal degradation during the preplastic state.

These results would suggest a hypothesis as follows:

The constituents which are so fluid at the plastic temperature as to form the plastic state by dispersing the nonfluid constituents with themselves consist of not only the constituents originally being small units in a fluid state at that temperature, but also the others produced from the larger molecular substances, which would not be extracted by usual organic solvents as real solution, by the thermal degradation.

According to these facts, it could be evidently explained that the caking properties depend on the nonextractable constituents as well as the extractable one in original coal.

The condensation reaction during the preplastic state was emphasized before and the decomposition is noted here, but it has been known that thermal decomposition of higher hydrocarbons, especially aromatics, is essentially accompanied with condensation.

As mentioned above, in spite of the almost same maximum fluidity, the sufficient differences of those temperatures certainly suggest the fact that the constituents referring to the caking power of each coal would differ in quality as well as quantity; the higher the temperature of the maximum fluidity, the more stable state the constituents have arrived at.

Further a hypothesis could be deduced from Fig. 8 which looks identical with Hoehne's work<sup>19)</sup> and the facts mentioned above as follows:

1) During the stage at which the maximum fluidity increases with rising of the temperature of the maximum fluidity, the constituents related to the caking properties are proceeding to the more stable state with an increasing amount of them.

2) During the next stage of the maximum fluidity lowering with elevating temperature of the maximum fluidity, the quantity of those constituents decreases as they convert to the more stable one.

The "most fusible state" of caking coal, as coal 4 to 7, is situated between the both stages, and the caking coal best suited for blast-furnace practice would be found in the higher temperature region of the maximum fluidity than that of the coal belonging to the "most fusible state".

3) In the last case, not so evident as the formers, the temperature of the maximum fluidity seems to sink with lowering of the maximum fluidity according to the advancing of the polymerizing degree up to such small units and large units as to decrease the quantity of the constituents related to the caking properties.

### 5. Influence of Addition of Coke Breeze upon Plastic Properties

It has long been known that the improvement of the coke occurs through the addition of coke breeze, and the addition of coke breeze as a factor in coke improvement is a great practical importance.<sup>20)</sup>

In Japan, the addition of semi-coke breeze has been carried out at the iron work in Hokkaido as mentioned already.

Any exact theories, however, supporting the fact that coke is improved through the addition of coke breeze have not been proposed yet.

Robert and Junkner<sup>20)</sup> emphasized that one of the most important advantages of blending inert fuel with coking coal undergoing carbonization was facilitated in accord with reducing the plastic layer. But it seems to be doubtful that the rapid heat penetration in coal charge would correspond to an improvement in qualities of coke from the coal as high in fluidity as coal 4 to 7. They also said that a number of coals rich in gas yielding a well fused coke, which in consequence of the lack of uniformity in the formation of the pores had poor physical properties, in most cases, showed an improvement in coke by reduction of the volatile matter.

J. G. King<sup>21)</sup> suggested that coke would behave as a diluent rather than a constituent and cokes containing over 15 percent of volatile matter appeared to combine more readily with the coking coal during melting or coking to form connecting layers or films containing both phases which were relatively strong.

Joh<sup>22)</sup> has recently suggested that the addition of coke breeze increased the strength of "cellulosic part" in coal substances, which was called "strength of the waist" in coal.

Here, the change of the plastic properties through the addition of coke breeze was determined by the plastometer method.

The coke added was produced in an iron retort which was charged with 200 grams of coal 4 and heated to 900°C at centre of the charged coal in a vertical electric furnace, and the rate of heating was 5°C per minute, the volatile matter was drawn upward and expansion of the charge was allowed against a load. The fraction, 35 to 65 mesh, of the crushed coke containing 3 percent of volatile matter was used.

As Fig. 13 illustrates the plastic curves sinking as a whole, the fluidity decreases with increasing amount of the coke added to reduce the plastic range, but the temperature of the maximum fluidity is hardly altered.

The relation of the maximum fluidity to the temperature range of the plastic state either with or without adding of coke breeze is shown in Fig. 14; all of these

points appear to dwell on the same curve. Therefore, through the addition of coke breeze the coals, which have the various maximum fluidity lower than the one of original coal but the temperature of the maximum fluidity as same as the one of original coal, could be obtained at will.

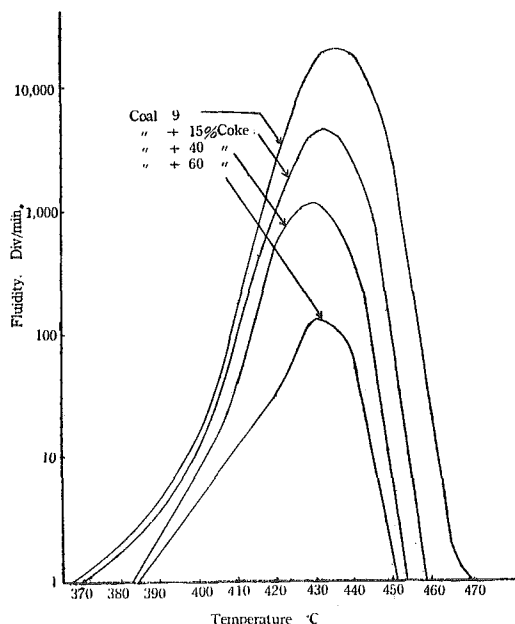


Fig. 13 Plastic Curves of Coal 9 Added with Coke.

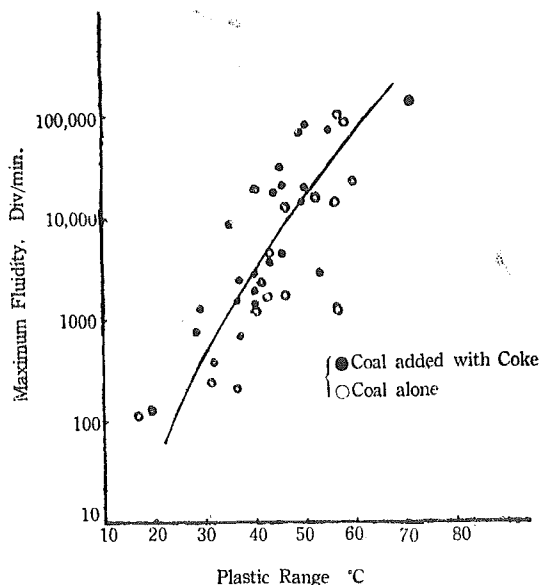


Fig. 14 Relation of Maximum Fluidity to Temperature Range of Plastic State.

The reducing values of maximum fluidity of the coals through the addition of the coke are plotted in Fig. 15. The decreasing rates are not the same for each coal; the rate of coal 6 is steeper than the one of coal 4. The curve of coal 18 especially differs from those of the coals having higher fluidity than itself.

Depending partly on the differences of ash content of the coals, this fact would also suggest that the constituents being in the liquid phase during the plastic state, as mentioned before, are not the same only in quantity but also in quality.

Furthermore, on account of the decreasing rate of fluidity on tar-pitch added with coke breeze at 100°C showing a very different shape from those obtained on the coals added with coke as in Fig. 15, it would be again expected that the plastic state of caking coal is not identical with the simple mixture consisting of an inert substance as coke and a liquid phase as pitch, but complex colloidal phase accompanied with thermal decomposition of coal substance.

The influence of size of the coke added upon the plasticity was observed by addition of the cokes, 65 to 100 mesh and passing through 100 mesh.

As in Fig. 16, the smaller the grain size of the coke added, the steeper is the decreasing rate. This fact could be explained by increasing of total surface of the

coke breeze added, with reduction of the size of the coke, to enlarge the amount of the liquid materials absorbed into the coke breeze and the frictional resistance between the plastic material and the coke.

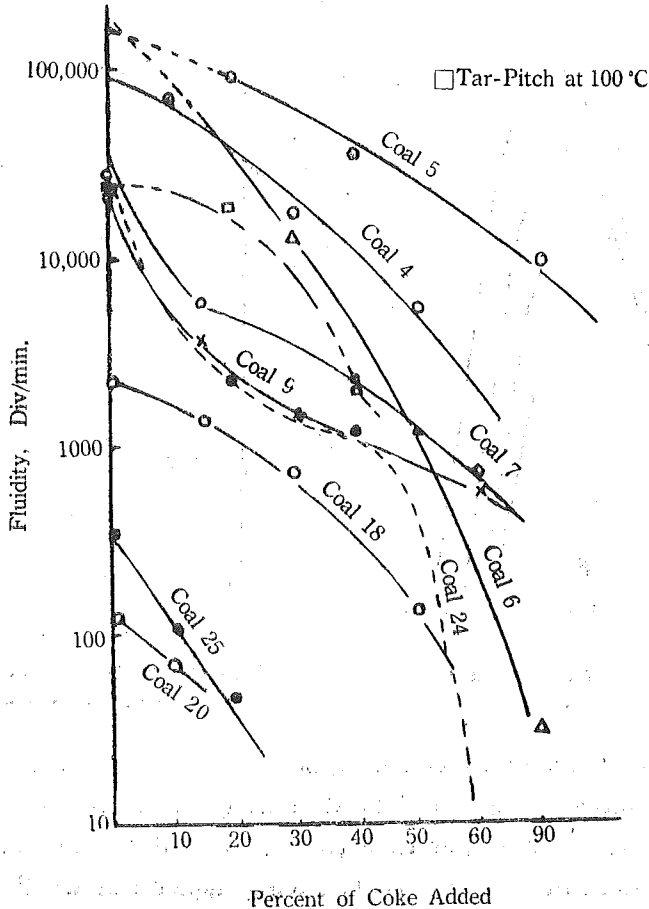


Fig. 15 Maximum Fluidity of Coals Added with Coke.

Some experiments through the addition of the sand heated for two hours with diluted hydrochloric acid were carried out. The rates of the decreasing fluidity, which occurred through the addition of the sand, are larger than those of the coke, in spite of that the total volume of the sand added is smaller than that of the coke at the same weight ratio of addition owing to larger specific weight of sand than that of coke breeze. In regard to this result, it seems to be a reasonable idea that the frictional resistance of coke breeze is less than that resulting from the addition of sand, thereby aiding by addition of coke breeze the surface of the coke grains becomes smoother by absorbing the plastic materials, which not present in the sand grains. From this idea it becomes evident that the coke added to cok-

ing coal absorbs the plastic materials during the plastic state.

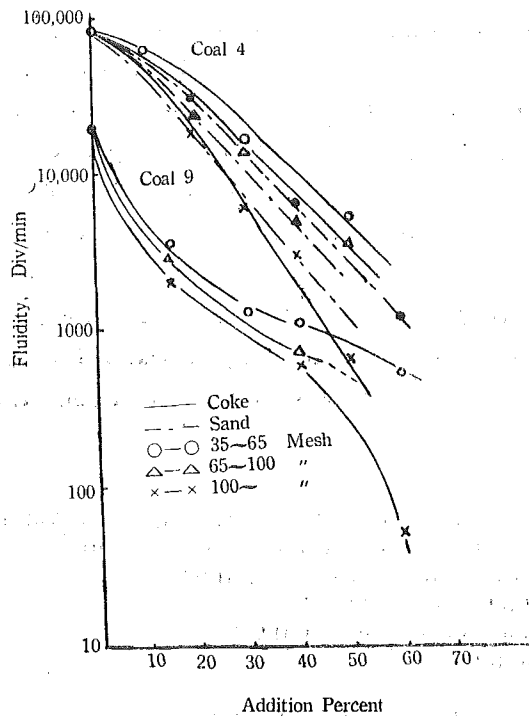


Fig. 16 Maximum Fluidity of Coals Added with Coke and Sand of Various Sizes.

Table VI

Influence of Addition of Coke, 15% V. M., and Electrode Carbon on Plastic Properties of Coal 4.

Percent of Addition	Coke, 15% V. M.				Electrode Carbon			
	35~65 Mesh		100 Mesh		35~65 Mesh		100 Mesh	
	30	50	30	50	30	50	30	50
Initial Softening Temp. °C	370	363	365	368	368	369	370	377
Fusion Temp. °C	416	411	415	416	405	411	407	414
Maximum Pointer Movement } Temp. °C	433	430	438	435	431	432	430	425
Div/min.	10,050	1,640	3,950	440	20,000	1,810	3,700	163
Solidification Temp. °C	456	447	458	448	460	450	450	439
End of Plastic Range °C	467	454	468	458	465	459	455	449
Plastic Range °C	40	36	53	32	54	39	43	25

Table VI shows the plastic properties of coal 4 added with the coke, having 15 percent of volatile matter, and electrode Carbon.

The decreasing of the maximum fluidity through the addition of this coke, 15

percent V. M., is somewhat larger than those of the coke, 3 percent V. M., and the electrode carbon in the case of the fraction, 35 to 65 mesh, but all the decreasing rates through the fraction, passing through 100 mesh, are almost similar to each other. Therefore, the size of the carbon added to the caking coal being below the limit which is about 65 mesh, the characteristics of the carbon substance added would hardly affect the plastic properties of the caking coal.

The relations of the facts mentioned above to the improvement in quality of coke through the addition of coke or semicoke breeze will be considered in the future paper.

In conclusion the author wishes to gratefully acknowledge the valuable aid of Professor Gan Takeya, the service rendered by Assistant Muraya Kamibayashi, and Shigeru Hayashi in development of this paper and to thank them accordingly for their cooperation.

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