

TABLE XIII. COMPARISON OF EXPERIMENTAL RESIN WITH COMMERCIAL RESINS
Application formulation (shoe sole)

Resin	Test Formula						
	A	B	C	D	E	F	G
Tensile							
12'/315° F.	1500	1450	1525	1750	1750	1475	1625
24	1675	1525	1400	1600	1475	1425	1700
Elongation, %							
12/315	290	300	390	370	320	250	430
24	305	275	395	340	360	370	405
Shore A							
12/315	90	83	84	85	87	87	72
24	88	83	84	86	85	86	73
Shore B							
12/315	70	63	64	65	67	67	52
24	67	63	64	66	65	66	53
Crescent tear B							
12	147	173	137	162	175	156	125
24	156	133	143	141	180	172	94
Ross flex, aged 24 hours, 212° F. oven, 0.250-inch sole							
12/315 cycles	250,046	65,000	201,643	250,046	90,061	250,046	250,046
Rating	5	10	10	2	10	3.5	9
24/315 cycles	287,587	169,000	287,587	287,587	42,210	196,560	166,000
Rating	1.5	10	5	2.5	5.5	10	10
Taber abrasion, H-22 wheels, 1000 grams, 500 rev., grams loss							
12 min.	0.411	0.368	0.275	0.405	0.302	0.386	0.252
24 min.	0.432	0.400	0.321	0.399	0.336	0.373	0.303
FORMULATION							
GR-S 26	50.00				Cumar MH 2½	7.00	
No. 1 smoked sheet	50.00				Paraffin	1.50	
Resin, as shown	50.00				Altax	2.00	
Calcium silicate	85.00				Methyl tuads	0.15	
Zinc oxide	5.00				Sulfur	3.00	
Process oil	5.00					258.65	

Crescent tear, A.S.T.M. D 624-48, Die B.

Hardness, A.S.T.M. D 676-42T.

Olsen flow, A.S.T.M. D 569-48.

Heat-Softening Point. A 1 × 3 × 0.075 inch test strip is placed over 1/16-inch diameter mandrels, placed 2 inches on center and supports a 143-gram weight having a specified presser foot, in a circulating water bath, the temperature of which is raised at the rate of 1° C. per minute. The temperatures are taken at the first deflection and when the sample is deflected 0.5 inch; the average of these temperatures is considered the heat-softening point.

Intrinsic viscosities, obtained by a conventional method, using 0.2 gram of resin in 100 ml. of benzene.

Taber Abrasion. Using Taber machine, the sample was tested after 500 revolutions using an H-22 wheel and 1000-gram weight.

Ross Flex. Ross flex, a standard of the shoe industry, was obtained on a 1 × 6 × 0.250 inch sample, cut with a 1/10-inch chisel awl perpendicular to the length at a distance of 2.5 inches from the attached end, aged for 24 hours in a 212° F. oven, and flexed on the Ross flex machine at the rate of 100 flexes per minute through an angle of 90°. The flex cut growth, measured in 0.1 inch, is given as the rating after flexing.

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Coal Hydrogenation Catalysts

STUDIES OF CATALYST DISTRIBUTION

Engineering
and
Process
development

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IN THE liquid phase hydrogenation of coal on a large scale, an attempt is usually made to achieve good distribution of the catalyst in the coal-oil paste. When the tin-ammonium chloride combination is employed, as in the Billingham plant of the Imperial Chemical Industries, Ltd., the tin is added in the form of tin oxalate, which is presumed to decompose under reaction conditions to give tin in a very finely divided state (3). Ferrous sulfate, when it was employed as a catalyst constituent in German plants at Pölitze, Blechhammer, and Gelsenberg, was impregnated on the coal from aqueous solution (7). There have been almost no

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published reports, however, of the significance of catalyst distribution for coal hydrogenation, and apparently no systematic study has been made of this subject. Almost all batch autoclave investigations of solid coal hydrogenation catalysts have involved the addition of powdered catalyst to the coal or coal-oil mixture (1, 2, 4-6, 10). In the case of one bituminous coal, a comparison has been made of powdered stannous chloride and stannous chloride impregnated on the coal (10). Very little difference was observed between the modes of catalyst addition at a concentration level of 1% tin; however, at lower concentrations (0.5 and 0.1% tin) superior results were obtained with the impregnated catalyst. It

This work was undertaken in order to learn more about the influence of the physical distribution of a catalyst on its effectiveness for promoting the hydrogenation of coal.

The activity of a number of catalysts was found to be much greater when they are impregnated on the coal from aqueous solution than when they are added as powders to the powdered coal. The ball-milling of coal and catalyst together was of intermediate effectiveness. With a Wyoming coal, the activity of stannous chloride was equaled by impregnated nickelous chloride and surpassed by impregnated ammonium molybdate plus sulfuric acid.

If careful attention is paid to the method of catalyst distribution, the effectiveness of many coal hydrogenation catalysts can be significantly improved. This may permit the utilization of cheaper and more readily available catalysts.

has now been found that differences in catalyst activity caused by differences in distribution are to be widely found in coal hydrogenation. The effect is occasionally very striking; in some cases, substances that are without catalytic effect when added as powders become equal or superior to the tin-halogen acid combination when impregnated on coal.

APPARATUS AND PROCEDURE

All of the experiments were carried out in rotating 1-liter autoclaves equipped with removable glass liners. The apparatus and procedures were identical with those previously described (9, 10). All catalyst tests were made under the following "standard" conditions: 450° C. reaction temperature, 1-hour reaction time at temperature, and 1000 pounds per square inch initial (cold) hydrogen pressure. Fifty grams of powdered coal were used in each experiment; in the experiments in which heavy-oil vehicle was added, 50 grams of vehicle were used.

The coal was impregnated with catalyst by immersing it in an aqueous solution of the catalyst, removing the bulk of the water by oven-drying at 110° C., and completing the drying in an oven at 50° C. In those experiments in which the catalyst was ball-milled with the coal, the ball-milling was continued for 6 hours. In the absence of either impregnation or ball-milling, the powdered catalyst was mixed with the coal only by tumbling in the rotary autoclave during the normal preheating period of 1.5 hours.

MATERIALS

Rock Springs coal from the D. O. Clark mine No. 9, Superior, Wyo., and Bruceton coal from the Bureau of Mines experimental mine at Bruceton, Pa., were studied. The heavy-oil vehicle was the product of a pilot plant run on the hydrogenation of Rock Springs coal; it contained 11.8% benzene-insoluble material, 39.3% asphalt (benzene-soluble, hexane-insoluble material), and 48.9% oil (hexane-soluble material). Ultimate analyses, on a moisture-free basis, of the two coals and the oil vehicle are shown in Table I.

TABLE I. ULTIMATE ANALYSES OF COALS AND OIL VEHICLE

Constituent	Rock Springs Coal, %	Bruceton Coal, %	Oil Vehicle, %
C	73.9	77.5	87.2
H	5.0	5.2	7.8
N	1.5	1.5	1.2
S	0.8	1.3	0.1
O (by diff.)	13.6	7.3	3.3
Ash	5.2	7.2	0.4

CATALYST TESTS

ROCK SPRINGS COAL TEST IN THE ABSENCE OF VEHICLE. Table II summarizes the results of catalyst tests with Rock Springs coal in the absence of vehicle. Under the conditions employed, when no catalyst is present Rock Springs coal shows the low liquefaction

of 33%. The term liquefaction is used here to represent the conversion of moisture- and ash-free coal to gaseous and liquid products, including asphalt. Addition of powdered ferrous sulfate (1% Fe) is almost without influence on the hydrogenation (run 1592). Impregnation of the coal with ferrous sulfate (1% Fe), however, causes a sharp increase in the liquefaction to 85%, with correspondingly high productions of asphalt and oil (run 1257). Part, though not all, of the potential catalytic effect of ferrous sulfate can be attained by ball-milling coal and catalyst (run 1357). Similar results are observed with nickelous chloride. Impregnated ferrous sulfate is as effective at a concentration of 0.5% iron as at the higher concentration, but much poorer results are obtained with 0.1% iron. The catalysis is not shown by all ferrous salts; ferrous chloride and ferrous bromide are very poor catalysts even when impregnated. This may be due to a poisoning effect of the halogen ion, as impregnation with ammonium chloride simultaneously with ferrous sulfate causes a great decrease in the catalytic activity of the ferrous sulfate (run 1568).

The behavior of nickelous chloride is very similar to that of ferrous sulfate. Added as a powder, nickelous chloride (1% Ni) is a very ineffective catalyst. Ball-milling with the coal increases its activity, and impregnation results in an activity at least as great as that of stannous chloride, previously considered to be the coal hydrogenation catalyst par excellence. Decrease in the nickel concentration to 0.5% causes a perceptible drop in extent of hydrogenation, and a decrease to 0.1% results in very poor catalysis. Impregnated nickelous sulfate is a moderately effective catalyst, but not as good as nickelous chloride. It is interesting to note that with iron, the sulfate has a higher activity than the chloride, whereas the reverse is true with nickel.

Impregnated stannous chloride gives results similar to those of impregnated nickelous chloride, the catalytic effect decreasing sharply as the concentration is decreased from 0.5 to 0.1% tin. At a concentration level of 1%, however, tin is exceptional, and possibly unique, in being almost as effective when added as powdered stannous chloride as when impregnated. The same result was observed earlier with Bruceton coal (9). The relative effectiveness of the powdered catalyst is much less at a concentration of 0.5% tin, whereas at 0.1% the catalytic effect is small for both powdered and impregnated catalyst.

Ammonium molybdate added as a powder was reported to be noncatalytic for the hydrogenation of both Rock Springs and Bruceton coal (10). Impregnation of the coal with ammonium molybdate, however, causes a striking increase in the extent of hydrogenation, liquefactions above 90% being observed (run 1436). German data (8) indicated that with low range (brown) coal, the catalytic effectiveness of ammonium molybdate is enhanced by neutralization of most of the alkaline ash of the coal with sulfuric acid. The coal in runs 1463 and 1523, Table II, was treated in this way; enough sulfuric acid was added to the aqueous solution of ammonium molybdate during impregnation to neutralize 90% of the "alkalinity" of the coal. The "alkalinity," defined as the weight of sulfuric acid neutralized by a given weight of coal, had been determined previously. Neutralization with sulfuric acid makes the effectiveness of impregnated ammonium molybdate even higher (run 1463). At a concentration of 1% molybdenum, a liquefaction of almost 95% is observed with Rock Springs coal under these conditions, along with an exceptionally low asphalt yield and an exceptionally high oil yield. The results are significantly superior to those obtained with stannous chloride at the same concentration of metal; they are the best the authors have ever observed with Rock Springs coal. In the absence of neutralization, the catalytic effect of impregnated ammonium molybdate drops sharply at concentrations below 0.5% just as in the cases of ferrous sulfate, nickelous chloride, and stannous chloride. Neutralization (90%) of the coal with sulfuric acid, however, causes a large increase in the liquefaction produced by impregnated ammonium molybdate at a concentration of 0.1% molybdenum (run 1523), although the con-

version of asphalt to oil is not as well catalyzed. The combination of sulfuric acid and impregnated ammonium molybdate is, in fact, by far the best catalyst for Rock Springs coal that has been tested in this laboratory.

Impregnation does not have universal effectiveness. As is to be expected, most materials that show no, or poor, catalytic activity when added as a powder are still poor catalysts when impregnated on coal. Among such materials are cobaltous chloride, zinc sulfate, and zinc bromide. In the case of certain insoluble catalysts, intimate ball-milling of the catalyst with the coal does produce some increase in activity (compare the results with ferrous sulfate above). Lead chloride is still ineffective when ball-milled with the coal, but lead bromide, which is a fair catalyst even when added as a powder, produces a liquefaction of 80% on ball-milling. The data suggest that lead bromide would be a highly effective catalyst if it could be impregnated on coal. Ball-milling also produces an increased activity in "copper chromite" (Adkins' catalyst), but this material is still a poor coal hydrogenation catalyst even under these conditions.

BRUCETON COAL TEST IN THE ABSENCE OF VEHICLE. The importance of catalyst distribution for catalytic activity has been verified in the cases of ferrous sulfate and nickelous chloride with Bruceton coal in the absence of vehicle. These experiments are summarized in Table III. Ferrous sulfate added as a powder has no appreciable effect on the hydrogenation of Bruceton coal, and powdered nickelous chloride is even a negative catalyst. For both materials, impregnation causes a marked increase in catalytic activity, the liquefaction rising to over 80%. Impregnated

TABLE II. EFFECT OF CATALYST DISTRIBUTION WITH ROCK SPRINGS COAL
(No vehicle)

Run No.	Catalyst	Mode of Distribution ^a	% of Moisture- and Ash-Free Coal			Gaseous hydrocarbons
			Liquefaction	Asphalt	Oil	
1228	None	...	33.4	2.8	10.4	9.0
1592	FeSO ₄ (1% Fe)	P	38.9	6.9	8.1	13.1
1257	FeSO ₄ (1% Fe)	I	84.9	38.9	21.7	15.0
1357	FeSO ₄ (1% Fe)	BM	66.2	24.1	21.2	11.4
1539	FeSO ₄ (0.5% Fe)	I	85.0	42.8	19.8	13.0
1535	FeSO ₄ (0.1% Fe)	I	53.0	17.7	10.4	13.7
1403	FeCl ₂ (1% Fe)	I	44.8	4.8	12.2	15.2
1402	FeBr ₂ (1% Fe)	I	50.4	7.7	17.9	12.4
1568	FeSO ₄ (1% Fe) + 0.5% NH ₄ Cl	I	52.1	14.8	13.8	13.7
1552	NiCl ₂ (1% Ni)	P	44.2	6.8	13.2	13.4
1336	NiCl ₂ (1% Ni)	I	88.3	15.5	45.3	18.0
1442	NiCl ₂ (1% Ni)	BM	56.9	17.2	19.3	10.4
1563	NiCl ₂ (0.5% Ni)	I	81.7	36.8	21.7	14.0
1494	NiCl ₂ (0.1% Ni)	I	47.5	8.3	15.9	12.0
1321	NiSO ₄ (1% Ni)	I	78.9	33.0	14.8	10.0
1598	SnCl ₂ (1% Sn)	P	82.3	26.5	29.2	14.5
1581	SnCl ₂ (1% Sn)	I	88.3	19.9	41.4	15.5
1393	SnCl ₂ (0.5% Sn)	P	67.9	23.4	20.0	13.4
1441	SnCl ₂ (0.5% Sn)	I	86.3	37.3	28.0	11.2
1391	SnCl ₂ (0.1% Sn)	P	52.3	17.1	11.4	12.5
1509	SnCl ₂ (0.1% Sn)	I	54.6	13.8	14.0	15.7
1121	AM ^b (1% Mo)	P	33.7	1.0	13.8	8.1
1436	AM (1% Mo)	I	92.7	27.2	41.1	13.6
1463	AM (1% Mo), neutralized	I	94.7	10.0	62.6	13.9
1446	AM (0.5% Mo)	I	89.4	28.4	37.7	13.8
1518	AM (0.2% Mo)	I	61.3	25.9	11.1	14.7
1493	AM (0.1% Mo)	I	53.4	14.9	14.9	12.7
1523	AM (0.1% Mo), neutralized	I	85.1	42.0	18.8	14.4
1310	CoCl ₂ (1% Co)	I	58.0	11.2	16.3	8.3
1314	ZnSO ₄ (1% Zn)	I	49.5	12.5	14.5	11.8
1389	ZnBr ₂ (1% Zn)	I	54.0	10.6	21.9	14.6
1292	PbCl ₂ (1% Pb)	BM	45.3	7.0	15.5	12.3
1361	PbBr ₂ (1% Pb)	BM	80.7	27.3	28.5	15.5
1504	PbBr ₂ (1% Pb)	P	71.1	28.6	20.7	12.6
1593	Copper chromite (2%)	P	42.2	7.4	9.1	13.6
1394	Copper chromite (2%)	BM	65.1	24.2	17.3	12.5

^a P, powdered catalyst added to charge; BM, catalyst ball-milled with charge; I, catalyst impregnated on charge.
^b AM, ammonium molybdate.

TABLE III. EFFECT OF CATALYST DISTRIBUTION WITH BRUCETON COAL

Run No.	Catalyst	Mode of Distribution ^a	% of Moisture- and Ash-Free Coal			
			Liquefaction	Asphalt	Oil	Gaseous hydrocarbons
1623	FeSO ₄ (1% Fe)	...	46.9	15.1	10.4	12.0
1245	FeSO ₄ (1% Fe)	P	55.6	27.1	14.2	10.4
1236	FeSO ₄ (1% Fe)	I	81.6	48.7	16.7	12.1
1259	FeSO ₄ (1% Fe)	BM	78.4	43.7	18.1	12.2
1453	FeSO ₄ (1% Fe)	Aq	68.4	36.1	13.5	15.2
1158	NiCl ₂ (1% Ni)	P	40.0	11.1	12.0	11.4
1362	NiCl ₂ (1% Ni)	I	82.6	28.3	36.7	15.0

^a P, powdered catalyst added to charge; BM, catalyst ball-milled with charge; I, catalyst impregnated on charge; Aq, aqueous solution of catalyst placed in autoclave with charge.

TABLE IV. EFFECT OF CATALYST DISTRIBUTION WITH ROCK SPRINGS COAL

Run No.	Catalyst	Mode of Distribution ^a	% of Moisture- and Ash-Free Coal			
			Liquefaction ^b	Asphalt ^b	Oil ^b	Gaseous hydrocarbons ^b
1506	None	...	64.9	47.0	-4.6	10.4
1469	AM ^c (1% Mo)	P	82.2	76.8	-17.7	12.7
1480	AM (1% Mo)	I	93.0	40.4	31.8	9.4
1486	NiCl ₂ (1% Ni)	P	39.4	13.5	4.0	10.2
1526	NiCl ₂ (1% Ni)	I	82.6	19.5	44.4	9.2

^a P, powdered catalyst added to total charge; I, catalyst impregnated on coal.

^b Corrected for contribution of vehicle.

^c AM, ammonium molybdate.

nickelous chloride is superior to ferrous sulfate for asphalt reduction, just as in the case of Rock Springs coal. Ball-milling of ferrous sulfate with the coal again results in a significant improvement, compared with the powdered catalyst, but not as much as is obtained with impregnation. An attempt to impregnate the coal in situ during hydrogenation gave rather poor results (run 1453).

ROCK SPRINGS COAL TEST IN PRESENCE OF VEHICLE. The experiments reported in Tables II and III demonstrate the importance of catalyst distribution under conditions when no oil vehicle is used. It was conceivable that a vehicle, if present, would distribute even powdered catalysts so well that the effects observed in the absence of vehicle would disappear. To investigate this point, several runs were made on the hydrogenation of Rock Springs coal in the presence of a coal hydrogenation heavy oil; the results are summarized in Table IV. The data given for product distributions have been corrected for the amounts of organic insolubles, asphalt, oil, and gas obtained when the vehicle alone is hydrogenated under the same conditions. As this procedure assumes that the hydrogenation of vehicle proceeds identically, whether or not coal is present, the corrections used can only be considered as approximate.

Comparison of run 1506 with run 1228, Table II, shows that in the absence of catalyst, a much higher liquefaction is obtained with Rock Springs coal in the presence of a vehicle than in its absence. This may be a real effect of vehicle or it may be due to the presence of traces of tin catalyst in the vehicle arising from the manner in which the pilot plant operation was carried out. The negative values for oil in runs 1506 and 1469 originate from the correction procedure discussed above. In addition, because of the empirical nature of the asphalt and oil analyses, the values for oil tend to be low whenever the quantity of asphalt is exceptionally large. This effect is especially great for run 1469.

In the presence of vehicle, the effect of catalyst distribution is qualitatively similar to that in the absence of vehicle, but there are quantitative differences. Powdered ammonium molybdate is appreciably catalytic (run 1469); even in this case, however, impregnation on coal markedly increases the liquefaction and in-

creases the conversion of asphalt to oil. Nickelous chloride gives striking results: Added as a powder, it behaves as a negative catalyst; impregnated on coal, it increases liquefaction and especially the asphalt-oil conversion.

It is clear that although the presence of vehicle changes the quantitative results obtained, catalyst distribution is still of major importance.

DISCUSSION

These experiments emphasize the role of catalyst distribution in determining activity. The more intimate is the contact of the catalyst with coal, the greater is the catalytic effectiveness; in fact, changing the mode of distribution in some cases changes the level of catalyst activity from a negligibly low to an extremely high value. It is, of course, not surprising that the intimacy of contact of catalyst with substrate should be of great importance, but it is a factor that has been at least tacitly overlooked in many studies of coal hydrogenation catalysts.

This work has several important implications. In the first place, for highest catalytic activity the best possible catalyst distribution should be sought. Unless experiments on a given coal-catalyst combination prove contrary, it would appear preferable either to impregnate the coal with catalyst from solution or, possibly, to spray the powdered coal with catalyst solution. The latter alternative would be more feasible in a large plant. This can be done, of course, only for catalysts that are soluble; in other cases extended ball-milling of coal and catalyst presents another, but not as effective, possibility.

Another result is that, for some coals, at least, the unique position of tin compounds as hydrogenation catalysts no longer exists. With Rock Springs coal, for example, impregnated nickelous chloride is as good as impregnated stannous chloride, and impregnated ammonium molybdate plus sulfuric acid is

definitely superior. Tin compounds are still peculiar in that, at high concentrations, they are almost as effective in powdered form as impregnated on the coal. However, this may be taken to mean that although a special mechanism, as yet not understood, exists that permits good distribution of tin compounds no matter how they are added, no special or unique character need be attributed to tin as a catalyst for the coal hydrogenation reaction proper. The mystery surrounding tin is thus pushed back one step, and it becomes less important for understanding the chemistry of coal hydrogenation.

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Engineering
and
Process
development

Polymerization Recipes for 41° F. Sugar-Free Redox Systems

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The development of sugar-free redox recipes for the polymerization of GR-S at 41° F. was undertaken in order to obtain simpler and more economical systems.

The activators studied in these recipes were: ferrous sulfate-potassium pyrophosphate complex which, however, still required a complicated make-up procedure; ferrous sulfide colloidal dispersion, in which the sulfide serves, not only to form a slightly soluble iron compound, but also to regenerate the ferrous iron as it is oxidized; ferrous soap dispersion, which is prepared in situ and works well only when the emulsifier is a fatty acid soap; ferrous silicate colloidal dispersion which works best with rosin-type emulsifiers and results in the simplest and most economical iron recipe hitherto developed; and polyethylene polyamines which have an advantage in ease of operation.

In the manufacture of synthetic rubber, these recipes afford simpler operation, better uniformity, economy, and freedom from pH drop on latex storage. Advantages to the

consumer are better uniformity of product at equal quality as compared with polymers from sugar-type recipes, particularly in carbon black master batches prepared from the latices.

AS EARLY as 1941, workers in the field of synthetic rubber recognized improvements in the physical properties of copolymers of the GR-S type prepared by polymerization of butadiene-styrene at low temperatures (1). However, at that time, the existing recipes were too slow for economical use. Consequently, since 1945, much work has been carried out by the various companies and universities in cooperation with the Office of Rubber Reserve to develop rapid polymerization recipes for use at 41° F. or lower. The first fast polymerization redox recipes were patterned after German recipes using benzoyl peroxide as the catalyst. However, this material was expensive and resulted in a polymerization with a rapid initial reaction surge which made temperature control rather difficult. At this time, the Hercules