produced 0.0054 gram of quinhydrone as compared with the blank. This reaction is evidently due to the oxidation of the hydroquinone in the presence of phenolase.

Alcoholoxidase

To 100 cc. of a 4 per cent ethyl alcohol solution neutralized with calcium carbonate to pH 7.2, 10 cc. of 0.5 per cent enzyme solution which had been boiled were added and incubated for 20 hours at 35° C. This experiment was also run using an active enzyme solution of the same strength, and the results were as follows:

		pH	pH after 20 hrs.' treatment
1	(Boiled enzyme soln.)	6.9	6.9
2	(Unboiled enzyme soln.)	6.9	6.4

The change of the acidity is apparently due to the formation of acetic acid by the action of alcoholoxidase on the alcohol.

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Effect of Fine Inerts on Agglutinating Power of Pittsburgh Coal[1,2]

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A study of the effect of addition of fine inerts on the agglutinating power of Pittsburgh coal has been made in which the test as modified by Marshall and Bird was used. A further modification of the method used by these writers in which electrode carbon was substituted for sand was also tried.

It is concluded that by the agglutinating-power test, as used by Marshall and Bird, the strength of the coked buttons obtained is increased by substitution of fine inert material up to 25 per cent of the coal under test. The effect varies somewhat with the character of inert used, but in every case an increase was found.

With the substitution of electrode carbon for the sand prescribed in the Marshall-Bird test, mixture of fine mineral inert with the coal used produced a weakening of the coked buttons obtained in the test, which, in the case of fusain, however, was slight for percentages under 20 per cent. This behavior of fusain was checked by actual coking tests on 80-pound charges.

THE term inert, as used here, will be understood to refer to substances separable from the coal by mechanical means which do not form a coke on destructive distillation. Thus all mineral matter occurring in the coal is inert in this sense, as is also fusain, or mineral charcoal. It is possible that there are organic constituents, other than fusain, making up the coal substance, which are inert, but so far this has not been proved. It is not necessarily true that such materials are inert in their effect on the strength of coke obtained from coal containing them; in fact, they may even improve the strength of the coke when admixed with the coal and coked under favoring conditions. Unquestionably it is of practical importance to know the effect of inerts on the coking property, because it is possible to regulate their amount in coal supplied for coke-making. The desirability of finding a simple laboratory test capable of measuring the effect of inerts on coke strength is thus evident. It has furnished the incentive for the work now to be described.

The purpose of the work was to apply a laboratory test to various synthetic mixtures of Pittsburgh coal with inerts occurring naturally in the coal and to determine, if possible, the applicability of the test for estimating their effect in coking power. The Marshall-Bird test (3) was selected for the work because it has been shown to give an approximate measure of the comparative coking power of coals. If this is true, then the test should also show the effect on coking power of adding different inerts in varying amounts to one and the same coal.

Coal and Inerts Used

The coal used in this work, as well as the samples of hard and soft fusains, was obtained from the Banning No. 1 mine of the Pittsburgh Coal Company, located near Van Meter, Fayette County, Pa. The proximate and ultimate analyses of the coal and the proximate analysis of the fusians are given in Table I.

Table I—Analysis of Banning (Pittsburgh Seam) Coal and Fusains Occurring Therein

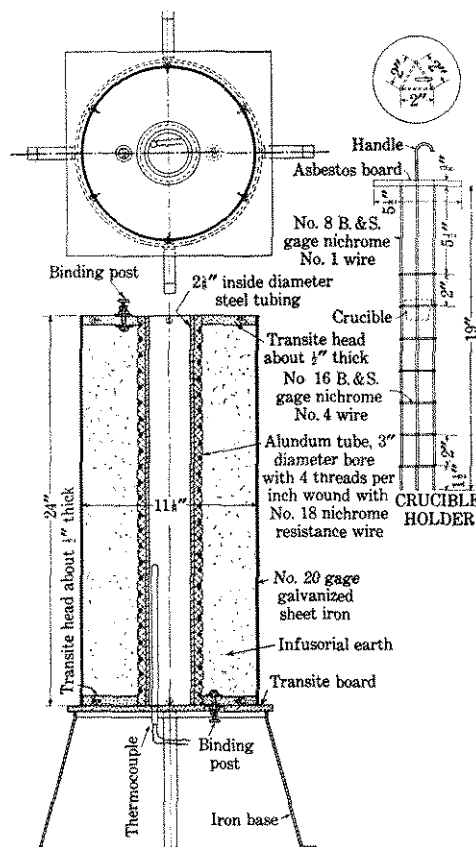| SAMPLE	MOISTURE	VOLATILE MATTER	FIXED CARBON	ASH	HYDROGEN	CARBON	NITROGEN	OXYGEN	SULFUR
	%	%	%	%	%	%	%	%	%
Coal	0.9	33.7	59.0	6.4	5.5	78.4	1.5	7.1	1.1
Soft fusain	2.1	11.0	78.9	8.0					
Hard fusain	0.4	17.3	54.8	27.5					

Figure 1—Furnace for Determination of Agglutinating Power

In some places the fusain found in this mine is hard and in other places it is so soft that it easily pulverizes on handling. The particular sample of hard fusain found contained 27.5 per cent of ash, 84 per cent of which was calcium oxide. The calcium oxide was present nearly entirely as calcium carbonate, as determined by analysis. The calcite, gypsum, and pyrite used were obtained from a local chemical supply house and sold as pure minerals. Before use they were ground to pass a 100-mesh screen. The sand was the same as that used as the diluting agent in the Marshall-Bird test. It was obtained from the Ottawa Silica Company, Ottawa, Ill.

The coarse sand called for in the Marshall-Bird test is an inert material, as is also the electrode carbon substituted for it in the modification of the method used. These materials are called diluents[3] in what follows to avoid confusion with fine inerts which are mixed with the coal in various proportions.

Apparatus and Procedure

The apparatus used is the same as that described by Marshall and Bird (3) except that the furnace was lined with a 2.63-inch seamless steel tube, as shown in Figure 1. On account of the high thermal conductivity of the steel, this tube promoted uniformity of the furnace temperature along the axis of the tube. This feature is important because five tests are made at a time in crucibles placed one above the other, and all must be subjected to the same heating conditions.

[3] Use of a diluent in this test is necessary because if 100 per cent coking coal were coked on this scale, a frothy coke entirely unsuitable for comparative-strength tests would be obtained. The term diluent, therefore, will refer to non-coking material added in sufficient amount to insure a compact coked mass suitable for testing. The proportion of diluent added is constant, and therefore the crushing strength of coked residues from various coals or mixtures should be proportional to their several coking powers.

The test procedure initially followed was the same as that recommended by Marshall and Bird, except that the coal used contained the stated percentage of fine inert matter before being mixed with the Ottawa sand used as a diluent. It is briefly as follows: Weigh out 22.727 grams of Ottawa sand sized to pass a 40-mesh and remain on a 50-mesh screen, and moisten thoroughly by mixing with 0.07 gram of glycerol. Then add the sample, which will consist of 2.273 grams of coal (or coal mixture containing the stated percentage of fine inert), mix thoroughly, level, and subject the contents of the crucible to a pressure of 6 kilograms for 30 seconds. The following will serve as an example of a charge containing 10 per cent of fine inert:

Weight of Ottawa sand, grams	22.727
Weight of coal, grams	2.046
Weight of fine inert, gram	0.227

The crucible, with the space remaining at the top filled with carbonized sand and coal from previous tests, is now placed in the electric furnace and carbonized at a temperature of 950° C. for 20 minutes. The coked button is removed at the end of the carbonization period and set aside for 24 hours, after which it is tested for crushing strength on the Riehle testing machine, shown in Figure 2. The crushing strength is recorded for each button, and the average of five or more buttons is taken as the crushing strength of the sample under test unless the strength of one of the buttons varies from this value by more than 10 per cent. In case a variation of this magnitude is found, further tests are made until all those of a series of five come within the 10 per cent limit.

Discussion of Results

The results obtained by following the method just described are given in Table II and shown graphically in Figure 3. There is no question but that addition of fine inert matter to Banning coal improves the strength of coked residue made under the specified carbonizing conditions.

Figure 2—Electric Furnace, Crucible Rack, and Riehle Strength-Testing Machine

The sand curve alone does not show strength improvement, but here the sand added to the coal was the same size as that used for diluting purposes—that is, it was sized 40 to 50 mesh instead of minus 100 mesh, as was the case with the other inerts. The other inerts behave somewhat differently among themselves, but in general the effect of addition of fine inert is to increase the strength of the coke obtained.

Dunn (1) has found exactly similar results to those of the writers as regards the effect of ash-forming minerals. He says:

Whilst it (the sand method) does enable one to classify roughly coals as to their coking properties, the method gives in many cases very anomalous results; and I have found in especial that a coal containing a very high percentage of ash has frequently shown a higher agglutinating power than a coal of the same origin containing less ash and obviously more desirable as a coking coal.

Table II—Effect of Inerts on Crushing Strength of Carbonized Buttons

(Ratio 10 parts of sand to 1 of coal plus inerts)

INERT	0%	10% Kg.	20% Kg.	30% Kg.	40% Kg.	50% Kg.	60% Kg.
Pyrite		8.12	8.16	7.73	6.82	3.39	
		8.09	8.78	7.58	6.04	3.00	
		7.73	9.23	8.26	6.38	3.10	
		7.84	8.48	8.48	6.68	2.60	
		7.97	9.54	7.27	7.24	3.20	
Av.		7.95	8.84	7.86	6.63	3.06	
Gypsum		8.22	9.56	8.32	7.09	5.50	
		8.87	9.63	8.67	6.95	5.59	
		8.62	9.62	7.97	6.98	5.31	
		7.62	9.52	9.42	6.97	6.14	
		7.10	9.01	8.36	6.92	5.98	
Av.		8.09	9.47	8.55	6.98	5.70	
Calcite		9.38	11.45	9.43	9.33	7.82	4.48
		9.22	10.25	9.05	9.27	7.18	4.36
		9.15	10.13	9.89	8.32	7.89	4.38
		8.82	11.25	10.28	9.38	7.38	4.51
		10.15	11.76	9.79	9.25	7.83	4.28
Av.		9.34	10.97	9.69	9.11	7.82	4.40
Hard fusain		9.26	13.12	12.11	11.74	9.76	6.06
		9.12	13.62	13.20	12.35	10.12	5.82
		10.63	12.08	13.85	11.53	9.47	6.18
		9.91	11.98	13.44	12.62	9.61	6.47
		10.50	11.64	14.23	11.20	8.54	6.06
Av.		9.88	12.49	13.35	11.89	9.50	6.11
Soft fusain		8.38	10.02	10.10	9.19	8.56	6.59
		9.07	11.12	10.08	10.24	9.24	6.87
		9.24	10.98	10.92	10.15	8.48	6.23
		9.56	11.53	10.73	9.15	8.42	6.84
		9.58	10.83	10.31	10.43	9.10	7.11
Av.		9.17	10.89	10.43	9.83	8.76	6.73
Coal and sand, same ratio as coal and sand in per cent column	6.67	6.07	6.86	5.15	3.08		
	6.86	7.23	6.98	4.92	3.00		
	6.84	6.98	6.89	5.24	3.30		
	6.89	6.84	6.91	4.81	3.47		
	6.73	6.67	6.02	5.08	3.44		
Av.	6.80	6.76	6.73	5.04	3.26		

Sinnatt (5) refers to Dunn's work and suggests that slagging of the sand with iron salts in the ash is probably the cause of high results with high-ash coals. He prefers electrode carbon as a diluent. With Sinnatt's suggestion in mind the writers tried to find proof of chemical action between the fine inerts and the sand without success. Coked mixtures were also examined, petrographically, in another laboratory of the United States Bureau of Mines for chemical action, with negative results.

The inert matter added to the coal was finely ground (minus 100 mesh) to facilitate perfect mixing with the coal. Kreulen (2) has measured the surface of various sizes (both sand and electrode carbons) used by him in tests of agglutinating power and found that the crushing strength of the cokes obtained varies widely with the size of the inert used. Furthermore, Mott and Wheeler (4) report that the addition of clean fine carbonaceous inerts to several varieties of English coals greatly improves the size of commercial cokes obtained from them. Recent unpublished carbonizing test results made in the United States Bureau of Mines laboratory show that an increase in ash content of from 9 to 16 per cent in the same coal greatly decreases the strength of coke made therefrom. However, in this case, the ash-forming minerals were coarse—from 0.25 inch to zero size. In this connection the results presented in Figure 4 are of interest. The data represented here were obtained merely by varying the proportion of coarse (40- to 50-mesh) diluent used. In one case the diluent was sand and in the other electrode carbon. The results show that if the inert used is coarse no improvement in the strength of the coke is obtained

by addition of more inert than that demanded in the Marshall-Bird procedure. They actually show a decrease in strength. Incidentally they show further that in the case of the electrode carbon there is a regular decrease in coke strength with increase of inert. The effect for Pittsburgh coal, at least, with sand is irregular. This would point to electrode carbon as the most appropriate diluent. The relatively rapid decrease in coke strength for the Pocahontas coal with increase of inert should also be noted. It can be seen that it makes considerable difference, in the case of the sand, what dilution ratio is selected for comparing the agglutinating power of these two coals. With electrode carbon the dilution ratio used does not affect the comparison nearly so much.
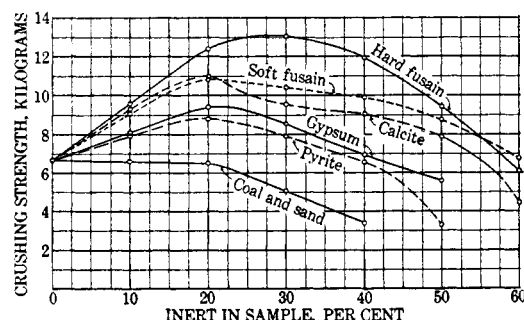

Figure 3—Agglutinating Values Using Sand as Diluent

Summarizing the preceding discussion, it is clear that substitution of fine inert materials for a portion of the Pittsburgh coal used here in the Marshall-Bird test increases the strength of the coked buttons obtained. This increase in strength is due very probably to the fineness (surface factor) of the added inert rather than to chemical action between inert and sand diluent, as has been suggested.

Table III—Crushing Strength of Electrode Carbon Buttons

(Ratio 14 to 1)

INERT	0%	10% Kg.	20% Kg.	30% Kg.
Pyrite		6.92	5.72	4.61
		6.52	6.03	5.22
		7.74	6.24	4.58
		7.55	6.83	4.87
		6.95	6.21	5.38
Av.		7.14	6.21	4.93
Gypsum		8.12	6.01	4.61
		7.18	5.82	4.49
		8.13	6.08	5.25
		7.21	6.63	4.74
		6.78	5.65	5.06
Av.		7.48	6.04	4.83
Calcite		6.68	5.43	3.86
		7.22	5.98	4.27
		6.81	5.65	4.33
		6.92	5.89	4.41
		6.26	4.81	4.31
Av.		6.78	5.55	4.23
Hard fusain		7.76	6.46	6.16
		7.29	6.92	5.06
		8.28	7.22	5.55
		7.61	6.02	5.78
		7.36	6.53	5.33
Av.		7.66	6.63	5.58
Soft fusain		9.24	8.57	7.02
		8.17	8.03	6.46
		8.08	7.78	6.32
		8.30	6.97	7.12
		8.18	7.91	5.52
Av.		8.39	7.85	6.49
Coal and electrode carbon, same ratio as electrode carbon and coal in per cent column	8.04	7.14	6.34	4.54
	8.77	7.23	5.51	4.67
	8.21	7.08	6.08	4.51
	8.71	7.97	5.38	4.98
	8.98	6.85	5.62	4.24
Av.	8.54	7.25	5.79	4.59

Use of Electrode Carbon Instead of Sand as Diluent in Marshall-Bird Test

Table III gives the results obtained by application of the Marshall-Bird test to Pittsburgh coal, wherein electrode

carbon is substituted for sand and the same mixtures of coal and inert previously tested with the sand diluent are used. Figure 5 gives the results graphically. The carbon was obtained from Acheson graphite electrodes by cutting on a lathe and sizing the cuttings to pass a 40-mesh and remain on a 50-mesh screen.
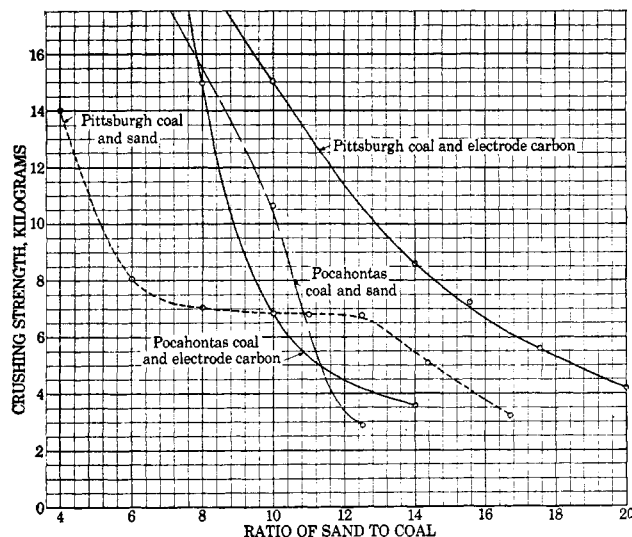

Figure 4—Variation in Crushing Strength of Coke with Varying Amount of Diluent Added to Coal Coked

In substituting electrode carbon for sand in the agglutinating test it was necessary to make a few minor changes, which are as follows: Because the density of sand is greater than that of electrode carbon, it was necessary to change the weight of the button to 15 grams. This made it approximately the same size as the sand button, and thus it was possible to use the same crucibles. Experiments proved that electrode carbon required 0.14 gram of glycerol to wet it, and that the ratio of 14 parts electrode carbon to 1 of sample, by weight, was the best suited to the limits of the strength-testing machine—that is, if a lower ratio were used, coals of higher agglutinating power than the Pittsburgh would not fall within the range of the machine. In all the other points the procedure was the same as described previously.

The curves of Figure 5 show that electrode carbon in the dilution ratio used gives a vastly different result from the sand in the ratio specified for the Marshall-Bird test. It is seen here that there is a regular decrease in strength with added fine inert other than fusain. Since with Pittsburgh coal a smaller dilution ratio than 14 to 1 can be used with the strength of the buttons still coming within the range of the testing machine, the same ratio as that used with the sand diluent was tried—that is, 10 parts of electrode carbon to 1 of the coal-inert mixture. Addition of 20 per cent gypsum at minus 100 mesh to the coal caused a drop in the strength of the buttons of 6 kilos, showing that even at this dilution ratio the fineness of added mineral inert has no specific effect, as was apparently the case with the sand diluent.

Large-Scale Tests

To obtain more conclusive data on the effect of pure fusain on the coking power of Pittsburgh coal, 80-pound charges of pure coal, coal plus 8 per cent of fusain, and coal plus 18 per cent of fusain, were coked in the bureau's standard carbonization test apparatus. Table IV gives proximate analyses of the coal and fusain.

Table IV—Proximate Analyses of Coal and Fusain

	MOISTURE %	VOLATILE %	FIXED CARBON %	ASH %	FUSAIN %
Pittsburgh coal	1.7	34.5	57.9	5.9	1.75
Fusain	2.1	11.0	78.9	8.0	

The mixtures of coal given in this table were carbonized at a temperature of 1000° C. It required approximately 5 hours and 45 minutes for complete carbonization.

The several cokes so obtained were subjected to the standard A. S. T. M. shatter and tumbler tests, the results of which are given in Table V.

Table V—Shatter and Tumbler Tests on Coke

	100% COAL %	92% COAL + 8% FUSAIN %	82% COAL + 18% FUSAIN %
	SHATTER TEST		
On 2 inch	32.5	33.6	29.8
On 1.5 inch	66.0	64.1	66.2
	TUMBLER TEST		
On 1.5 inch	5.0	4.3	8.2
Fines	32.0	28.2	32.3

Table VI contains the proximate and ultimate analyses of the coke, also heating value, apparent and true specific gravity, and the cell space.

Table VI—Proximate and Ultimate Analyses of Cokes

	100% COAL %	92% COAL + 8% FUSAIN %	82% COAL + 18% FUSAIN %
	PROXIMATE ANALYSIS		
Moisture	0.26	0.1	0.1
Volatile	0.86	0.9	1.6
Fixed carbon	87.97	87.8	87.2
Ash	10.91	11.2	11.1
	ULTIMATE ANALYSIS		
Hydrogen	0.87	0.6	0.6
Carbon	85.80	86.1	86.3
Nitrogen	1.28	1.1	1.1
Oxygen	0.38	0.1	0.1
Sulfur	0.76	0.9	0.8
Ash	10.91	11.2	11.1
B. t. u.	12,630	12,830	12,820
Apparent sp. gr.	0.87	0.89	0.92
True sp. gr.	1.9	1.91	1.90
Per cent of cell space	54.2	54.5	51.4

It is seen that there is practically no difference in the strength of the cokes (Table V), which is in accord with the curve for fusain given in Figure 5. The chemical analyses of the cokes are nearly identical (Table VI). The apparent specific gravity increases with increase of fusain. With the true specific gravity remaining constant as it does, it is obvious that the cell space will decrease with increasing per cent of fusain.
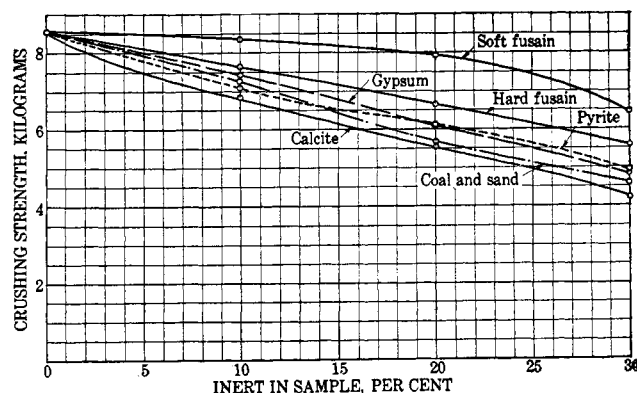

Figure 5—Agglutinating Values Using Electrode Carbon (Ratio 14 to 1)

The preceding results obtained with Pittsburgh coal indicate that when the inert used in the agglutinating-power test is entirely carbonaceous, fineness does not have a specific effect, but that, when the diluent as well as the added inert is mineral matter, fineness does have a specific effect. Clearly there must be further investigation of the various factors involved in the test before it can be applied with any confidence to the solution of practical problems relative to coke quality. Furthermore, it seems probable that in order to compare coals as to strength of coke which may be obtained from them, several dilution ratios, instead of one, will be

required to obtain a reliable value for the agglutinating power. This applies at least to the use of the sand diluent.

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Color in Fertilizers[1]

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Colors in fertilizer materials are discussed. A study was made of three methods of coloring synthetic fertilizer materials: by adding a concentrated dye solution to a melt of the material to be colored, by adding the dye solution to a strong solution of the material and evaporating to dryness with stirring, and by thoroughly mixing a small amount of concentrated dye solution with the dry material. Each material was satisfactorily colored violet, blue, green, yellow, and red. The cost of dye required varies from 7 to 58 cents per ton of material colored. The triphenylmethane dyes proved the most satisfactory of the several classes tried.

FERTILIZER materials can be conveniently classified into three groups according as they are derived from mineral deposits, industrial wastes, or atmospheric nitrogen. The materials of the third group differ from those of the other two in that they are white or nearly white, while those of the other two groups vary greatly in color.

Materials obtained from mineral deposits owe their color to the presence of pigmented impurities or to their association with salts that have the characteristic property of selectively absorbing or reflecting different light rays. Most of the organic wastes used as fertilizers are even more highly colored than the mineral fertilizers, owing to the presence of a pigment, such as carbon, or to such dyes as chlorophyll, xanthophyll, and carotin. The color associated with most of the fertilizer materials of the first two groups is usually sufficiently characteristic to serve as a means of distinguishing between them. The materials of the third group, on the other hand, are usually lacking in characteristic features, particularly when granulated. Artificial coloring has therefore been proposed as a convenient means of readily differentiating between such materials as are without marked distinguishing characteristics.

According to a French patent issued to I. G. Farbenindustrie (1), a colored fertilizer has been obtained by adding 1 to 3 parts of a substantive dye or the leuco form of a vat dye to 10,000 parts of a melted fertilizer composed of ammonium nitrate and calcium carbonate. Among other examples given in this patent is one in which a concentrated dye solution is added to a 45 per cent solution of sodium nitrate, and the mixture evaporated to dryness.

The coloration of fertilizers offers a convenient means of studying segregation in fertilizer mixtures, and the primary purpose of the work outlined in this paper was to facilitate the study of methods for preventing this undesirable feature of mixed fertilizers. Methods are described for giving a range of colors, including red, yellow, blue, green, and violet, to some of the more common synthetic fertilizer materials. Data are also included on the amount and cost of the dyes used in giving characteristic colors to fertilizer salts. No tests were made on the use of pigments for coloration of fertilizers, owing to the relatively large quantity required to give a characteristic color.

Experimental Data

Suitable methods of imparting color to fertilizer salts vary with the chemical and physical properties of the material. In the commercial production of fertilizer materials, certain steps in the various processes of manufacture offer opportunities for the addition of a coloring agent, and in many cases the addition of the dye is the only extra step necessary to obtain a colored product. In this investigation a study was made of three methods of coloring: by adding a concentrated dye solution to a melt of the material to be colored, by adding a dye solution to a strong solution of the materials and evaporating to dryness with stirring, and by thoroughly mixing a small amount of a concentrated dye solution with the dry material.

The principal considerations influencing the selection of dyes for this work were high tinctorial power, solubility in water, stability under the conditions involved, low cost, and availability. The quantities of dyes given in Table I are expressed in terms of strengths most commonly encountered, and the costs are calculated on that basis. The dye names used are those of the pre-war prototypes, and each dye name is accompanied by its Colour Index number (2),[2] which serves to distinguish and identify it at all times.

For convenience in measuring the quantity of dye employed and because of differences in dye content and tinctorial power of the various dyes employed, the strengths of the aqueous dye solutions varied between approximately 0.01 and 0.1 per cent. In large-scale work such dilute solutions would not be necessary. The materials to be colored included neutral, acid, and alkaline compounds. They contained such bases as lime, potash, and ammonia, and such acid radicals as phosphate, sulfate, and nitrate. All the colored final products were screened to the same particle size in order to facilitate color comparison.

Coloring Melts

The method of coloring melts is limited to materials, such as urea, Calurea, and calcium nitrate, which melt at temperatures below that at which the dye used in the process would decompose.

In the coloring of these compounds, the desired quantity of standard dye solution was added, and the material was heated just to the melting point and then allowed to recrystallize with continuous stirring.

Coloring from Solution

Potassium nitrate, potassium chloride, and monoammonium phosphate were selected as materials having suitable solubili-