

is comparatively concentrated. However, with properly prepared Nessler reagent, this latter trouble should not occur.

Experimental work was undertaken with the object of developing a more accurate method of determination as a result of which a modification of the above mentioned method was adopted. By this modification of the method, the sample and standard distillates are prepared under similar conditions, and when treated with Nessler reagent develop colors identical in quality or tone, but proportional in intensity to the ammonia present.

If the Nessler reagent is carefully prepared and works properly, the color in sample and standard will develop almost instantly and is fully developed in less than one minute. The solutions treated with such Nessler reagent remain clear or do not cloud appreciably on standing for ten minutes; however, the comparison is best made after standing one minute and all possible difficulty due to clouding avoided.

The determination is also rendered more accurate by taking a larger sample for analysis and using an aliquot part of the total distillate for comparison.

The reagents are prepared exactly as described in Blair's "Chemical Analysis of Iron," seventh edition.

[NOTE—The ammonia-free hydrochloric acid may also be prepared thus: Dilute concentrated hydrochloric acid to specific gravity 1.10 and, without addition of sulfuric acid, distil it. Hydrochloric acid of this strength distills without change in concentration. The first 100 cc. distillate from one liter of acid will usually contain all the ammonia and is rejected; the portions distilled thereafter are collected for use but must, of course, be tested as usual to make sure they are free from ammonia.]

#### METHOD OF DETERMINATION

**DISTILLATION OF SAMPLE**—In a distilling flask of 1000 to 1500 cc. capacity, fitted with separatory funnel and connected with condenser, place 40 cc. prepared caustic soda solution; add 500 cc. distilled water, and distil until the distillate gives no reaction with Nessler reagent.

Dissolve a 5 g. sample of the steel in 40 cc. of ammonia-free hydrochloric acid, and by means of the separatory funnel add the solution slowly to the contents of the distilling flask, washing in finally with ammonia-free water. Distil and collect 150 cc. of the distillate in a graduated flask. Cork the flask and set aside. Experience has shown that 150 cc. of distillate will contain all the nitrogen in the sample.

**PREPARATION OF STANDARD**—After distilling the sample—the apparatus then being free from ammonia, but containing the residue of sample and reagents—25 cc. of standard ammonium chloride solution and 150 cc. of ammonia-free water are added to the contents of the flask, and distillation continued until a *standard* distillate of 150 cc. is collected in a graduated flask. As before, the single distillate will be found to contain all the ammonia from 25 cc. of standard solution.

To the standard distillate is added 6 cc. of Nessler reagent; and since the standard ammonium chloride solution is equivalent to 0.00001 g. nitrogen per cc., 1 cc. prepared standard distillate is equivalent to  $\frac{25 \times 0.00001}{156} = 0.0000016$  g. nitrogen per cc. = 0.00016 per cent nitrogen on a one gram sample.

It should be noted that the preparation of a single standard distillate is sufficient for determination of nitrogen in several samples if the comparisons are being made at the same time.

**COMPARISON AND DETERMINATION**—To make the determination, 30 cc. of *sample distillate* (equal to *one gram* of sample) are placed in one of a pair of Nessler jars and the color developed by addition of 1 cc. Nessler reagent. The standard and sample are allowed to stand one minute to fully develop the color.

Into the other jar the standard distillate is run from a burette until the colors in standard and sample jars are of the same intensity; the final comparison is made after bringing the contents of the jars to the same volume by addition of ammonia-free water to one or the other.

The number of cc. standard distillate multiplied by 0.00016 gives the percentage of nitrogen in the steel.

PERCENTAGES OF NITROGEN FOUND							
No.	N	No.	N	No.	N	No.	N
1.....	0.0038	4.....	0.0032	7.....	0.0038	10.....	0.0035
	0.0037		0.0032		0.0043		0.0035
	0.0037	5.....	0.0043	8.....	0.0037	11.....	0.0033
2.....	0.0035		0.0043		0.0040		0.0038
	0.0035	6.....	0.0040	9.....	0.0038		0.0037
3.....	0.0037		0.0040		0.0043		0.0037
	0.0037		.....		.....		.....

The results shown in the above table indicate the accuracy of the method thus modified.

TITANIUM ALLOY MANUFACTURING CO.  
NIAGARA FALLS, N. Y.

## ADDRESSES

### THE INDUSTRY OF THE COAL-TAR DYES<sup>1</sup> AN OUTLINE SKETCH

By BERNHARD C. HESSE  
Received October 29, 1914

At the very beginning, it should be pointed out that the world's market in coal-tar dyes as it stands today comprises, in round numbers, 900 distinct and different chemical substances which are made by the aid of 300 products of transformation, themselves not dyes, of 10 products obtained or obtainable from coal-tar by distillation, refrigeration, expression or the like. Therefore, actually and in reality, the present coal-tar dye industry comprises no fewer than 1,200 different products and as

<sup>1</sup> Address delivered before the Board of Directors of the General Chemical Company, in New York, October 23, 1914.

many or more different processes of manufacture and requires many hundred different sets of apparatus of varying capacities and of differing kinds for many hundred different operations. A manufacturing problem comprising so many independent and yet interlaced units of manufacture and production has, therefore, varied elements of complexity; to what extent this is true will appear later on.

#### THE NATURE OF COAL-TAR

In the production of coal-tar, suitable for use in the coal-tar dye industry, there is made on the average from 100 parts of coal: 72 parts COKE 6 parts TAR (liquid and solid distillate) 22 parts GAS

The gas and coke are not considered here; the distillate, amounting to 6 per cent of the weight of the coal, is the portion of these products with which we are here concerned.

Chemists have ascertained the presence of 155 distinct chemical substances in this liquid and solid distillate or tar; these classify broadly, as follows:

SERIES	No.	SERIES	No.
Marsh gas.....	45	Anthracene.....	5
Benzol.....	73	Phenanthrene.....	5
Naphthalene.....	14	Miscellaneous.....	13

For dyestuff production the first is negligible and the last almost so. The number of chemical elements entering into the composition of the above substances is relatively small, being five only:

CARBON    HYDROGEN    OXYGEN    NITROGEN    SULFUR

According to the combinations of these elements, we have the 5 following classes of compounds:

Carbon and hydrogen.....	76
Carbon, hydrogen and nitrogen.....	37
Carbon, hydrogen and oxygen.....	23
Carbon, hydrogen and sulfur.....	3
Carbon, hydrogen, nitrogen and sulfur.....	3

Rearranging these under the three relevant general series we have:

	Benzol	Naphthalene	Anthracene	TOTAL
Carbon and hydrogen.....	25	6	3	34
Carbon, hydrogen and nitrogen.....	32	..	2	34
Carbon, hydrogen and oxygen.....	11	8	..	19
Carbon, hydrogen and sulfur.....	3	..	..	3
Carbon, hydrogen, nitrogen, and sulfur.....	2	..	..	2
TOTAL.....	73	14	5	92

Out of these 92 compounds the coal-tar dye industry uses only 9, namely:

Benzol	Phenol	Methyl anthracene
Toluol	Naphthalene	Phenanthrene
Xylol	Anthracene	Carbazol

These nine make up about from 6 to 12 per cent of the liquid and solid distillate, or from 0.38 per cent to 0.75 per cent of the coal taken, divided approximately as shown in the following chart (Fig. I) from Dammer, "Chemische Technologie der Neuzeit," Vol. 2, p. 906. The percentages there given are as follows:

	On tar	On coal
Benzol, toluol, etc.....	1.75	0.105
Phenol.....	0.25	0.015
Naphthalene.....	5.95	0.375
Anthracene, etc.....	0.20	0.012

These figures are average and, therefore, illustrative only and not strictly accurate in all cases.

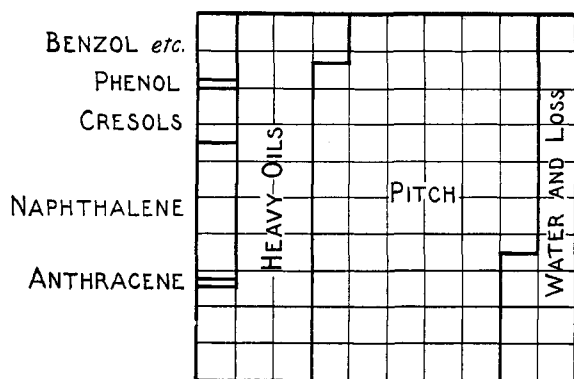


FIG. I.—MAIN CONSTITUENTS OF COAL TAR

Fig. II is a graphic representation of the above relations between the products obtained by the destructive distillation of coal and the coal itself.

None of these solids and liquids are themselves dyes; in fact, most, if not all of them, are substantially colorless and cannot impart color.

The entire coal-tar dye industry is based upon these 9 coal-tar compounds, or crudes; these 9 crudes are converted into about 300 intermediates, themselves not dyes, and these 300 intermediates are turned into 900 and more dyes.

#### THE SCOPE OF THE INDUSTRY

World's figures are not available. The most dependable and most recent figures are those dealing with Germany. In

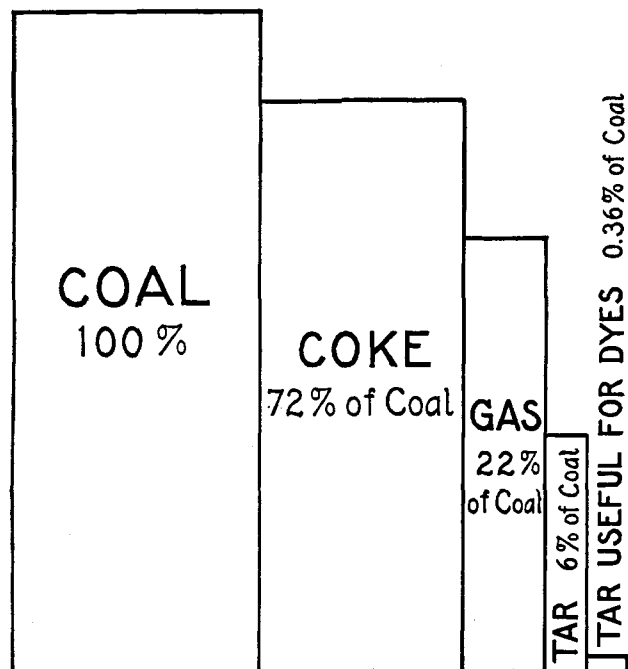


FIG. II.—COMPARISON OF COAL AND ITS DISTILLATION PRODUCTS

the year 1913 the total export value of Germany's coal-tar industry, including dyes and products of chemical transformation of the above 9 crudes themselves not dyes, *i. e.*, intermediates, amounted to \$55,264,522, distributed over 33 countries and shared in by 22 factories. On June 30, 1912, 21 of these factories had a combined capitalization of \$36,700,000 and declared and paid dividends of \$11,600,000, or 21.74 per cent of the capitalization.

Of the 5369 active corporations in Germany on June 30, 1912, 1004, or 18.69 per cent, are divided into 19 groups of the chemical and allied industries. Arranged in the order of their income-producing effects these 19 groups are, in part, as follows:

	Per cent dividends	No. of corporations
Coal-tar dyes.....	21.74	21
Metallurgy.....	11.78	61
Soaps and candles.....	11.65	21
Glass.....	11.61	38
Heavy chemicals.....	11.51	104
Explosives.....	11.22	28

The remainder range between 5 and 10 per cent except mining which is at the foot of the list with 0.51 per cent return.

Therefore, any attempt to take away coal-tar dye business from Germany means attacking the best equipped and the most profitable of Germany's industries.

**PLANT VALUE**—The actual cost of construction of the various plants engaged in coal-tar dye manufacture cannot be determined with any accuracy. All sorts of estimates and guesses have been made ranging from \$50,000,000 to \$1,000,000,000 with the majority in the neighborhood of \$400,000,000.

**ANNUAL TURNOVER**—The annual turnover cannot be determined exactly, but assuming that Germany consumes twice as much as the United States imports, we have a putative turnover of about \$80,000,000 or 2.1 times the capital stock.

The supervision and control of making this \$80,000,000 worth of product, requires at the utmost 1000 works or factory chemists, *i. e.*, on the average, one works or factory chemist for each \$80,000 of annual output.

The gross of \$55,264,552 export value is distributed over more than 900 finished dyes, each chemically different from the other and each requiring a separate though allied manufacture. This amounts to an annual average of \$61,405 for each dye all over the world outside of Germany.

However, we must subtract \$18,534,964 from the \$55,264,552 for the indigo, alizarin, anilin oil and various things, not dyes, to obtain the value of the 900 dyes which is \$36,729,588; or, an average annual world's gross, outside of Germany, of \$40,811 for each of the 900 dyes.

**LARGE ITEMS OF MANUFACTURE**—The large items of these 900 dyes as nearly as can be ascertained from official sources of exports are:

	Value	Per cent of total	Per cent of total exports to U. S.
Indigo.....	\$12,690,874	23.01	10.38
Alizarin.....	2,219,588	3.99	8.05
Anilin oil.....	1,408,722	2.54	33.42
Anthracene dyes.....	2,914,786	5.22	44.08
Anilin dyes.....	33,814,802	61.24	21.56
Anthracene and benzol compounds not dyes.....	1,492,736	2.72	16.22
Naphthalene compounds, not dyes.....	723,044	1.27	20.53

The dyes, including indigo, alizarin, anthracene dyes and anilin dyes, are sold to 33 countries distributed as shown in Table I.

TABLE I—GEOGRAPHICAL DISTRIBUTION OF GERMANY'S EXPORT DYE-TRADE (PERCENTAGES)

	Anilin dyes	Alizarin	Anthracene dyes	Indigo	
EUROPE (19)					
Great Britain.....	17.14	24.34	23.72	3.54	
France.....	2.15	1.59	2.52	0.97	
Portugal.....	0.65	...	...	...	
Spain.....	1.02	...	...	0.20	
Italy.....	6.38	...	3.23	1.98	
Austria.....	8.99	3.38	6.80	4.08	
Turkey.....	0.68	...	...	0.33	
Roumania.....	0.35	...	...	...	
Servia.....	0.15	...	...	...	
Bulgaria.....	0.20	...	...	...	
Greece.....	0.10	...	...	...	
Switzerland.....	1.22	4.23	...	...	
Russia.....	1.71	2.83	3.17	1.30	
Finland.....	0.37	...	...	...	
Norway.....	0.42	...	...	...	
Sweden.....	1.40	...	0.73	...	
Denmark.....	0.37	...	...	0.03	
Netherlands.....	2.12	3.09	2.76	1.83	
Belgium.....	3.90	...	1.96	0.94	
ASIA (6)					
Japan.....	5.45	...	1.63	2.46	
China.....	13.17	...	...	64.03	
British India.....	5.35	39.89	4.44	0.97	
British Malacca.....	0.22	...	...	0.36	
Dutch East Indies.....	0.38	8.41	1.49	2.86	
Persia.....	...	...	...	0.18	
SOUTH AMERICA (3)					
Argentina.....	0.25	...	...	...	
Brazil.....	0.98	...	...	...	
Chili.....	0.09	...	...	...	
NORTH AMERICA (3)					
Canada.....	0.69	...	...	0.25	
United States.....	21.55	8.03	44.10	10.38	
Mexico.....	0.85	...	...	0.05	
AFRICA					
Egypt.....	0.34	...	...	1.33	
AUSTRALIA					
Australian colonies.....	0.16	...	...	0.47	
					Average participation
RECAPITULATION					
Europe.....	49.32	39.46	44.89	15.20	37.22
Asia.....	24.57	48.30	7.56	70.86	37.82
South America.....	1.32	...	...	...	0.33
North America.....	23.09	8.03	44.10	10.68	21.47
Africa.....	0.34	...	...	1.33	0.42
Australia.....	0.16	...	...	0.47	0.16
Totals.....	98.80	95.79	96.55	98.54	97.42

Germany buys small quantities of dyestuffs from six countries (probably as the United States buys eggs and butter from Canada) as shown below:

GERMANY'S 1913 IMPORTS OF INTERMEDIATES AND FINISHED DYES

	Value	Per cent of total exports
Anilin oil and salt.....	\$ 31,654	2.25
Naphthol and naphthylamine.....	30,940	4.28
Anthraquinone nitrobenzol, toluidin, resorcin, phthalic acid and other coal-tar products.....	116,620	7.81
Anilin dyes.....	1,415,388	4.17
Alizarin red and all other anthracene dyes.....	179,452	3.49
Indigo.....	92,582	0.73
TOTAL.....	\$1,866,636	3.79

#### THE WORLD'S PRODUCTION OF COAL-TAR DYES

In 1896 the world's *anilin* (*i. e.*, only a part of the coal-tar dyes) dye production was estimated at \$25,000,000 distributed as follows:

		Per cent
Germany.....	\$18,000,000	72
Switzerland.....	3,200,000	12.8
France.....	1,600,000 to 2,000,000	8.0
Great Britain.....	1,600,000 to 1,800,000	7.2

This is *exclusive* of alizarin, anthracene dyes and of indigo.

For 1912, value figures are available only for Germany, Switzerland and Great Britain; tonnage figures for Austria. They show the following trade balance in *all* branches; crudes, intermediates and finished dyes, inclusive of anilin dyes, alizarin, anthracene dyes and indigo.

FINAL BALANCES, 1912		Imports	Exports
Germany.....			\$51,545,326
Switzerland.....			3,794,898
Great Britain.....	\$6,275,775		

The distribution of these balances over the various items is shown in Table II.

#### AVERAGE UNIT PRICES OF CRUDES, INTERMEDIATES AND FINISHED DYES

If the following 1912 tables for Germany, Switzerland and Great Britain are recalculated to cents per pound for each subdivision, in the case of benzol the prices per U. S. gallon are:

British export values =	16.75 cents
German import values =	24.20 cents
German export values =	19.11 cents

The average German import and export values of crudes, intermediates and finished dyes in 1913 was as follows:

	IMPORTS		EXPORTS	
	Cents per lb.	On basis of crudes	Cents per lb.	On basis of crudes
Crudes.....	2.06	1.00	2.83	1.00
Intermediates.....	12.08	5.85	10.07	3.56
Finished dyes.....	23.57	11.42	21.53	7.61

These average figures, unfortunately, give no direct insight into the true enhancement of crudes to intermediates, to finished dyes. While these crudes are as a rule of quite uniform percentage purity, yet the intermediates and the finished dyes are not; some of the intermediates contain only 60 per cent of the theoretical of the corresponding crudes, some of the finished dyes, *e. g.*, indigo, being in the form of 20 per cent pastes with water. This foregoing relationship is, therefore, directive only and *not* quantitative, *i. e.*, it does not represent the actual enhancement per pound of crude or of absolute intermediate to absolute finished dye. A nearer approach to true enhancement of crudes to intermediates is made further on in the case of anilin, naphthol and naphthylamine.

#### ENHANCEMENT OF CRUDES TO INTERMEDIATES

As a matter of mere calculation and making no allowance for losses, etc., 889 lbs. of naphthalene make 1000 lbs. of naphthol or of naphthylamine, and 839 lbs. benzol make 1000 lbs. of anilin oil.

Based on the averages of the corresponding German figures of Table III there is a margin of 10.40 cents per lb. of naphthylamin or of naphthol over the naphthalene cost, to take up the cost of the nitric acid, sulfuric acid, iron, muriatic acid, and caustic soda and other expenses, which amount is practically 7.6 times the naphthalene item. For anilin oil there is a corresponding margin of 6.15 cents per lb. to take up the nitric acid, iron and muriatic costs and other expenses, which amount is only 2.7 times the benzol item.

Enhancement in the anthracene series cannot be deduced from these figures.

TABLE II—DYE PRODUCTIONS IN 1912

GERMANY				GREAT BRITAIN			
CRUDES				Exports			
Benzol and light oils.....	\$ 508,844	\$ 1,630,538		Benzol and toluol, gals.....	4,579,667	\$ 918,568	
Naphthalene.....	184,450	211,106		Carbolic acid, cwt.....	162,459	1,006,008	
Anthracene.....	66,402	12,138		Naphthalene, cwt.....	54,312	110,203	
Phenol.....	536,928	851,802		Anthracene, lbs.....	2,938,098	37,872	
Cresol.....	7,616	72,352					\$2,072,651
TOTALS.....	1,304,240	2,777,936					
INTERMEDIATES				Exports			
Anilin oil and salt.....	4,284	1,558,662		Anilin and toluidine, lbs.....	1,429,130	\$ 155,702	
Naphthol and naphthalene.....	41,412	681,870					\$ 155,702
Anthraquinone, nitrobenzol, resorcin, phthalic acid, etc.....	106,624	1,432,998					
TOTALS.....	152,320	3,673,530					
FINISHED DYES				Imports			
Anilin dyes.....	1,424,192	31,835,832		Cwt.		Dollars	
Alizarin.....		2,197,216		Anilin and naphthalene dyes.....	283,876	7,025,619	
Anthracene dyes.....		3,428,866		Alizarin and anthracene dyes.....	61,178	1,285,870	56,728
Indigo.....	120,904	10,760,932		Indigo.....	28,302	436,138	982,675
TOTALS.....	1,672,426	48,222,846		All other synthetic dyes.....	190	1,757	
EXCESS				TOTALS.....	8,729,224		982,675
Crudes.....		\$ 1,473,696					
Intermediates.....		3,521,210					
Finished dyes.....		46,550,420					
BALANCE.....		\$51,545,326					
AUSTRIA (values not given)							
CRUDES				Imports			
Distillation products of coal-tar.....	1,004	2,739		Cwt.		Dollars	
Carbolic (crude).....	54	159		Anilin and naphthalene dyes.....	283,876	7,025,619	
Carbolic (refined).....	170	14,965		Alizarin and anthracene dyes.....	61,178	1,285,870	56,728
Naphthalene (crude).....	259	15,607		Indigo.....	28,302	436,138	982,675
Anthracene (crude).....		1,111		All other synthetic dyes.....	190	1,757	
TOTALS.....	1,487	34,581		TOTALS.....	8,729,224		982,675
INTERMEDIATES							
Anilin oil.....	4,290	2					
Anilin salts.....	4,805	2					
Nitrobenzol.....	1,242	8					
TOTALS.....	10,337	12					
FINISHED DYES							
Alizarin, anthracene dyes and synthetic indigo.....	19,382	5,635					
Azo and sulfur dyes.....	46,546	133					
All other coal-tar dyes.....	11,695	1,664					
TOTALS.....	77,623	7,432					
EXCESS							
Crudes.....		33,094					
Intermediates.....	10,325						
Finished dyes.....	70,191						
BALANCE.....	47,422						

Enhancement of intermediates to dyes cannot be stated from these figures with any approach to utility and is, therefore, not attempted.

TABLE III—AVERAGE UNIT PRICES (CENTS PER LB.) OF CRUDES, INTERMEDIATES AND FINISHED DYES

	GERMANY		SWITZERLAND		GREAT BRITAIN	
	Imp.	Exp.	Imp.	Exp.	Imp.	Exp.
CRUDES						
Benzol, toluol, etc.....	3.28	2.59	No classifica-			2.27
Carbolic, crude and refined...	3.48	8.63	Average is			6.19
Naphthalene.....	1.40	1.14	5.51	5.70		2.03
Anthracene.....	1.29	0.78				1.29
INTERMEDIATES						
Anilin oil and salts.....	9.19	8.80				
Anilin oil.....			8.89	7.96		
Anilin and toluidine.....					10.29	
Naphthol and naphthylamin.....	12.93	10.55				
Anilin compounds.....			22.68	32.10		
Benzyl, chlorid, nitrobenzol, naphthol, etc.....			12.95	31.33		
Phthalic acid and resorcin.....			25.84	54.41		
Anthraquinone, nitrobenzol, toluidine, resorcin, phthalic acid, etc.....	12.96	11.38				
FINISHED DYES						
Anilin dyes.....	24.82	23.86	29.93	31.87	24.75	
Alizarin.....		16.42	12.70			
Anthracene dyes.....	13.50	26.93				
Alizarin and anthracene dyes.....	(a)	(a)			21.02	
Indigo.....	72.14	17.26			15.41	
Indigo and carmine.....			18.14	18.82		
All other synthetic dyes.....					9.25	

(a) Import is vegetable and dry; export is 20 per cent paste.

GERMANY'S 1913 FOREIGN TONNAGE MOVEMENT  
The 1913 metric tonnages of Germany of crudes, intermediates and finished dyes are:

Metric tons	IMPORTS	EXPORTS
Crudes.....	17,400	51,318
Intermediates.....	673	16,321
Finished dyes.....	3,238	108,680
TOTALS.....	21,311	176,319

The total tonnage movement is, therefore, 197,630. For every ton imported, Germany exports 8.27 tons; for every dollar Germany imports, she exports \$20.46.

## ESTIMATED WORLD'S TOTAL COAL-TAR DYE PRODUCTION, 1912

The export values of coal-tar dyes for 1912 at hand are:

Germany.....	\$48,222,846
Switzerland.....	5,452,651
Great Britain.....	982,675
TOTAL.....	\$54,658,172

A very liberal estimate of the production of the principal countries is about as follows:

United States.....	\$ 3,750,000
France.....	5,000,000
Great Britain (over exports).....	5,000,000
Switzerland (over exports).....	1,000,000
Germany (over exports).....	20,000,000
	\$34,750,000

This makes ample allowance for all items and gives a grand total of \$89,408,172, or practically \$90,000,000, as the very

maximum of *all* coal-tar dyes, anilin dyes, alizarin, anthracene dyes and the like and indigo produced by the five leading countries in 1912.

Thus the following is the *estimated* distribution of total production:

Germany.....	\$68,222,846
Great Britain.....	5,982,675
Switzerland.....	6,452,651
France.....	5,000,000
United States.....	3,750,000

with Russia, Holland, Austria and Belgium to be added. Allowing \$10,000,000 for these, which is clearly very high, makes the absolute maximum production all over the world substantially \$100,000,000. The combined actual factory or works area of the world's coal-tar dye plants probably does not exceed one square mile.

#### GERMANY'S ALLEGED DEPENDENCE FOR COAL-TAR MATERIALS UPON FOREIGN COUNTRIES

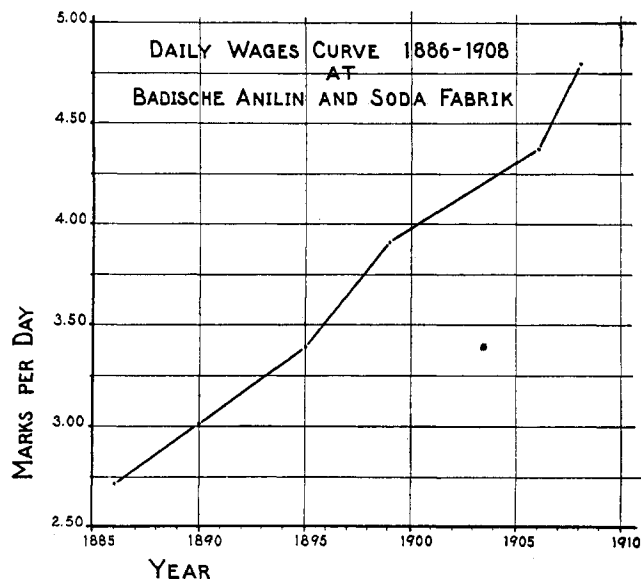
It has been urged that Germany is not wholly independent of outsiders for its coal-tar materials; possibly so. The foregoing 3.79 per cent of imports to exports may support that view.

By the same token the United States is dependent upon outsiders for hay, eggs, wheat, cotton and copper. For the years 1908-1914, both inclusive, the corresponding U. S. figures (low, average and high) are as follows:

	Low	Average	High
Hay.....	5.28	186.83	623.20
Eggs (1908-1912 only).....	1.68	6.06	12.63
Wheat.....	0.05	1.65	7.77
Cotton.....	3.19	3.60	4.24
Copper.....	24.24	31.89	36.95

#### THE WAGE QUESTION

In 1908 the average wage paid in Germany in this industry was about 4.80 marks per day inclusive of boys, common labor and skilled labor. With about 24 boys out of every 100 persons employed, and assuming each boy receives on the average  $\frac{1}{4}$  a man's pay, this makes the average man's wage M. 5.85 or \$1.40. Adding to this, \$750,000 annual welfare expense for a



total of 7000 employees and refiguring on the above ratio, makes the daily allowance for this item per man at 300 days per year 44 cents additional or a total of \$1.84, average daily adult wage. To this should be added the bonuses given to many of the workmen and also the works' contribution to the state old age pension and sick fund. Consequently, the average adult daily wage is actually in the vicinity of \$1.84.

This is reinforced by the detailed Table IV of the year 1906, wherein 40.32 per cent receive less than \$1.00 per day and 59.68

per cent receive more than \$1.00 per day of ten hours, with a grand average of \$1.04 per ten-hour day.

TABLE IV—THE BADISCHE ANILIN AND SODA FABRIK WAGE TABLE OF ABOUT 1906

Apart from bonuses, welfare expense and accident, insurance and pension fund

Daily pay in cents	Aliz-arin	Anilin fac-tory	Azo dye fac-tory	Acid and soda fac-tory	Indigo fac-tory	Con-struction de-part-ment	Machin-ery de-part-ment	Totals
78.5	2	23	...	...	6	8	...	39
80.9	1	8	...	2	30	...	...	41
83.3	2	31	21	50	55	2	42	203
85.8	23	52	54	81	75	49	11	345
88.2	15	39	31	72	71	3	13	244
90.5	15	49	57	72	87	36	25	341
92.9	11	32	55	72	52	5	30	257
95.3	19	30	50	72	54	73	29	327
97.7	46	35	68	64	74	15	54	356
100.1	62	70	68	73	66	161	71	571
102.4	55	48	53	71	31	26	121	405
104.8	94	78	47	41	9	36	14	319
107.2	74	58	42	37	5	19	38	273
109.6	25	16	21	21	2	15	59	159
112.0	11	13	23	19	...	38	67	171
114.3	1	12	12	13	...	39	71	148
116.7	9	7	3	...	...	18	22	59
119.1	...	10	5	...	...	93	47	155
121.5	1	6	1	...	...	30	19	57
123.9	...	3	...	...	...	88	35	126
126.3	...	2	...	2	...	56	29	89
128.6	...	...	...	...	...	95	23	118
131.0	...	...	4	...	...	107	19	130
133.4	...	...	...	...	...	33	31	64
135.8	...	...	...	...	...	19	18	37
138.2	...	4	...	...	...	28	31	63
140.5	...	...	6	...	...	2	22	30
142.9	...	...	...	...	...	16	13	29
145.3	...	4	...	15	...	7	21	47
147.7	...	...	6	...	...	8	19	33
150.1	...	...	...	...	...	6	6	12
152.4	...	...	...	...	...	12	19	31
154.8	...	...	...	...	...	...	6	6
157.2	...	...	5	...	...	4	...	9
159.6	...	...	...	...	...	6	3	9
162.0	...	...	...	...	...	7	...	7
164.3	...	...	...	...	...	2	...	2
166.7	...	...	15	...	...	8	...	23
176.1	...	...	5	...	...	...	...	5
Total employees	466	630	652	777	617	1170	1028	5340
Gross pay roll in dollars	473	620	659	740	567	1372	1166	5597
Average day pay in dollars	1.01	0.98	1.01	0.95	0.92	1.17	1.13	1.04

NOTE—These figures assume payment for ten hours only, although the men work in shifts from 6 A.M. to 6 P.M. for day work, and from 6 P.M. to 6 A.M. for night work. If the pay is for 12 hours, then each of these figures for average day, pay being based upon *hourly* wage-rate, must be increased 20 per cent over their present values, i. e., they would become \$1.21, \$1.18, \$1.21, \$1.14, \$1.10, \$1.40, \$1.36 and \$1.25, respectively.

#### THE INCREASED COST OF LABOR IN GERMANY

The following table presents the figures per head per working day (i. e., boys, skilled and common labor):

	Marks	Dollars	Per cent
1886.....	2.71	0.645	100.0
1890.....	3.01	0.716	111.1
1895.....	3.38	0.804	124.8
1899.....	3.91	0.926	144.3
1906.....	4.37	1.040	161.3
1908.....	4.80	1.142	177.0

or an average annual increase of 3.5 per cent of the 1886 pay.

However, it must be remembered that in Germany the day is a two-shift day with two hours and twenty minutes taken out for all men for meals and rest and for about one-third the men an additional thirty minutes for washing up; so that one-third work twelve hours less two hours and fifty minutes, and two-thirds work twelve hours less two hours and twenty minutes, or an average day of  $9\frac{1}{2}$  hours net actual average working time for which they receive at least ten hours pay and it may be twelve hours pay; the above figures, as stated, were based on hourly rate of pay assume pay for ten hours, only, and *not* for twelve hours.

In the United States the day is a three-shift day.

#### PARTICIPATION OF LABOR CHARGE IN FINISHED DYES

Labor participates to a small extent only in the final cost of the finished dye; it probably never exceeds 15 and is, as a rule, more nearly 10 per cent.

As an illustration: in 1906, Germany's export of synthetic indigo was worth about \$4,750,000; the 617 men in the Badische

indigo factory made at least 50 per cent of that export value, or \$2,374,000 worth. These 617 men represent a daily pay roll of not more than \$678.70, and it may be as low as \$567.50 (dependent upon pay being for twelve hours or ten hours); at 365 days per year this means \$247,725 or \$207,137, or 10.43 or 8.72 per cent, respectively, on half of the above indigo export value; *assuming* bonuses, welfare expenses and the like to *double* that daily pay roll, it makes the labor participation 20.86 and 17.44 per cent, respectively; however, this frees the indigo manufactured and consumed in Germany from *all* labor charges.

However, these 617 men no doubt in 1906 had a greater participation than 50 per cent of the export and it is, therefore, reasonable to assume that 15 per cent participation by labor in the finished product is ample and very likely high.

#### A TYPICAL GERMAN COAL-TAR DYE FACTORY

A German coal-tar dye works in good order and of considerable magnitude will have a daily use for 1000 tons of coal, 40 tons ice, 40,000,000 gallons of water (about  $\frac{1}{7}$  of Manhattan and the Bronx), 2,500,000 cu. ft. of gas.

The works area is about 500 acres, of which 100 acres are occupied by buildings, and requires about 42 miles of railway within the factory walls to transport the various materials among the several hundred factory buildings.

Power generation and transmission require 158 boilers, 386 steam engines and 472 electric motors. Over 400 telephones are needed within the works.

In order to convert the nine products obtained from coal-tar into intermediate products, and then into dyes, these works need, as auxiliary chemicals: sulfuric acid, hydrochloric (muriatic) acid, nitric acid, liquid chlorine, caustic soda, carbonate of soda, acetate of soda, acetic acid, acetic anhydrid, bromine and iodine—in large amounts, which, for obvious reasons, cannot be distributed as to the total amounts produced or used.

The following figures, taken from Dr. Brunck's 1900 Indigo Lecture, may give an idea of the magnitude of some of these items; these figures are now more than 14 years old and have no doubt immensely increased; at that time the Badische Anilin and Soda Fabrik made about 50 per cent of the world's consumption of indigo. Today all the German works make practically 95 per cent of the world's consumption; it is fair to double the following figures to get an approximate notion of today's figures; 50,000 tons of sulfuric anhydrid (equal to 40,000 tons pyrites), 4,400,000 lbs. of glacial acetic acid, which require not less than 5,200,000 lbs. liquid chlorine and produce 5,850,000 lbs. caustic soda as well, and the equivalent of about 7,800,000 lbs. or 3,900 tons of commercial muriatic, and an investment of \$4,500,000.

At that time (1900) the total world's consumption was estimated at 11,000,000 lbs. dry weight (100 per cent) indigo; in 1913 Germany *exported* 15,000,000 lbs. (100 per cent) indigo.

The world's annual consumption of indigo is today not far from 8200 tons (100 per cent) indigo or 27 tons per day.

#### PATENTS AND THE COAL-TAR DYE INDUSTRY

The development of the coal-tar dye industry called for 8062 German patents in the years 1876-1912, or 224 per year; corresponding patents have been taken out in other countries, *e. g.*, 2432 in the United States.

But it is authoritatively said that only 1 in 100 of the German patents is a money maker and, as a matter of fact, in the case of the 921 dyes in the world's markets at the end of 1912, only 485 U. S. patents and 762 German patents were involved, or 19.94 per cent of the total U. S. and 9.46 per cent of the total German patents. Of these 921 dyes, 50 per cent, were never patented in the United States; the U. S. patents on 26 per cent have now expired leaving 24 per cent still covered by existing U. S. patents, but many of these expire in 1915.

#### THE PRIMARY COAL-TAR PRODUCTS AND THE INTERMEDIATE PRODUCTS

The nine different crudes from coal-tar which form the basis of the coal-tar dye industry are first converted into materials, themselves not dyes, but different from the nine original compounds. These nine compounds make about 270 intermediate products and these 270, by suitable combination, make the 900 and more different dyes of the present world's markets.

The above number of intermediate products by no means exhausts those that are possible, nor do the 900 dyes exhaust those theoretically possible; there are probably over 2000 intermediate products possible, but only about 270 that have found use and there are many thousands of millions of dyestuffs wholly distinct from each other embraced in the 8,000 German patents; but of these thousands of millions of dyes only 400 individuals have survived and are of use. It is extremely doubtful that in the remainder of these millions upon millions there are any dyes of any striking utility not covered by those already in use. It is safe to say that the German coal-tar dye industry has gone over all of the known fields in fine-tooth-comb fashion and the results thereof are laid down in their patents and are shown in the goods that they market. The Germans are, of course, searching for new fields; in the last 10 years only one new field has been opened and while that is limited it promises to be of great value.

#### THE FUNCTION OF RESEARCH IN ESTABLISHING THE PRESENT INDUSTRY IN THE U. S.

Therefore, a research laboratory, in the narrow sense of the word, is not necessary for the development of a real coal-tar dye industry in the United States. What we *do* need is a semi-manufacturing laboratory in which to ascertain the most favorable conditions for carrying out those operations which the work of the Germans both in their patents and in their commercial exploitation of them has shown to be needful or worthy of prosecution. That, however, is no child's play task; it calls for engineering skill of the highest order, for chemical knowledge of great refinement and experimental ability of high rank. Much will have to be learned and determined as to the proper materials of construction, the proper size and shape of the apparatus and the most favorable working unit, which is by no means constant from one dyestuff or one intermediate product to another. Many dyestuffs cannot be made commercially in lots much greater than 110 pounds; others can be made in lots of one ton, but the manufacturing unit, as a rule, is small. Much of this apparatus is enamelled or homogeneously lead-lined.

Of course, the ultimate success will depend upon our merchants and our ability to merchandize against the very efficient merchandizing organization of the Germans.

#### •MANUFACTURING PROCESSES

It must not be assumed that the precise manufacturing directions are all laid down in the literature, patent or otherwise. Practically all of the works keep the details of their actual processes very much to themselves. Thus, for example, one works may excel in the production of sulfonated anilin-blues; while there is nothing patented or patentable about that operation, the trade will take one factory's product in preference to any other, on looks or "aspect" alone. There are numerous instances where even these large German works with all their research facilities and with all their engineering ability have been unable to outflank an original patentee or original producer, either as to price or as to quality of the goods whose patent has expired, even years after the expiration of that patent. This has also occurred in the case of non-patented products and in one instance, at least, Americans can and do produce a dye from German intermediates and sell that dye back to the Germans at a price and of a quality the Germans cannot meet. We must, therefore, be prepared to expect that our goods would not sell in open competi-

tion with foreign makes of the same good; for perhaps one or more years after we had attempted to market them.

#### ACQUIRING PROCESSES

Furthermore, on account of the necessity of having good, careful, uniform manufacture at all points it is quite out of the question for any one chemist to acquire valuable manufacturing experience, except in only a very limited number of chemical transformations. Therefore, successful purchase of recipes or engagement of competent manufacturing chemists to make whole lines of dyes is practically out of the question although it may succeed for a limited number of dyes or operations. We shall have to rely on our own ingenuity, skill and ability to devise successful commercial methods of manufacture.

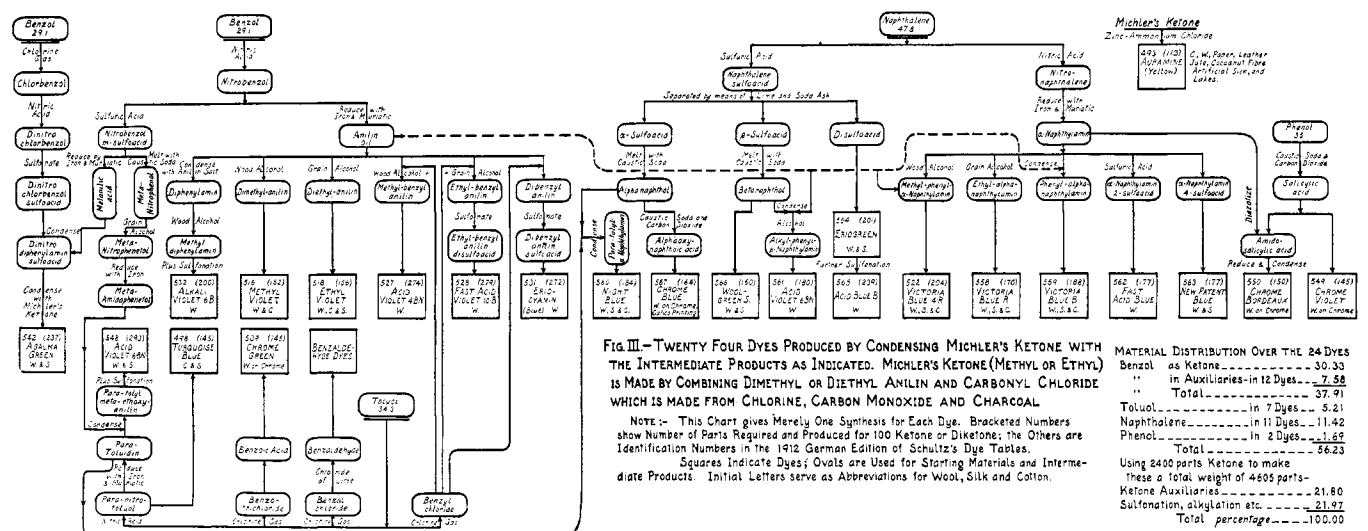
#### THE MARKETING OF COAL-TAR DYES

In 1897 the total number of different brands or commercial varieties of dyes sold by a single German concern all over the world amounted in round numbers to 8,000. Each one of these 8,000 brands has its own peculiar advantage over each of the others. These 8,000 brands, which have, no doubt, increased in number now, are used by those who use dyestuffs and produce with them thousands upon thousands of different shades and tints upon materials of the greatest diversity. This necessitates, of course, the constant production of sample cards by the

diagrams have been constructed to show in the simplest and most direct manner the genetic relationships between crudes, intermediates and finished dyes; these charts are, therefore, *not* to be taken as expressing all details or all possible modes or even the very best modes of making the various products and transformations. What they are intended to express is the order of production of the principal transformations and to indicate very briefly merely the outline of *one* way of accomplishing that change; they are indicative or directive only and are by no means to be regarded as presenting complete actual manufacturing operations or anything approaching that.

#### THE KETONE DYES (FIG. III)

This synthesis has been selected for the purpose of illustrating a group of twenty-four dyes closely related chemically, as well as from a manufacturing point of view; they are all good sellers and have been in the world's markets for upwards of 30 years with the exception of one or two which are only 8 or 10 years old. Eight were never patented in the United States. On 11 the U. S. patents have expired, on 3 the U. S. patents expire in 1915 and one each in 1916 and 1925. They represent only  $\frac{1}{40}$  of the entire number of dyes but exemplify and typify the interlocked and interlaced manufacturing dependency as simply as possible. Other groups are far more complex, chemically



dyestuff-makers each season of each year to show how the fashionable shades and even staple shades can be made profitably and cheaply.

#### BY-PRODUCTS

Broadly speaking, the entire coal-tar dye industry is a complicated maze and net-work of interlocking and interlacing products and by-products; these are great in number but, in most cases, small in volume individually. In numerous instances the very existence of the by-products was the sole directing cause for the invention of new dyes and classes of dyes.

#### THE DYES OF THE WORLD'S MARKETS

The 921 different dyes on the world's markets at about the end of 1912 are divided into 17 separate chemical classes as follows:

Nitroso dyes.....	4	Chinolin dyes.....	4
Nitro dyes.....	4	Thiobenzenyl dyes.....	5
Stilbene dyes.....	10	Indophenol dyes.....	1
Pyrazolone dyes.....	12	Oxazin and thiazin dyes.....	48
Azo dyes.....	462	Azin dyes.....	38
Auramines.....	2	Sulfide dyes.....	52
Tri- and di-phenylmethane dyes.....	73	Anthraquinone and allied dyes	116
Xanthone dyes.....	34	Indigo dyes.....	48
Acridin dyes.....	8		
		Total.....	921

#### THE CHARTS OR DIAGRAMS

For present purposes of illustration a number of charts or

as well as from the point of view of manufacture and sale. Fig. III probably represents the simplest and least complex relations in the coal-tar dye industry.

It should be remembered that each of the 17 different classes is interlaced and interlocked with one or more other classes and that the interlacing between individuals of Fig. III is true in great and very important measure of the 17 large divisions.

"KETONE"—The starting material for the 24 dyes of Fig. III is called "Michler's Ketone" and is prepared from dimethyl anilin and carbonyl chloride. It was discovered in 1876.

Dimethylanilin is made from anilin, anilin salt and acetone-free wood alcohol; anilin itself from nitrobenzol and that from benzol and nitric acid.

Carbonyl chloride is made from equal volumes of carbon monoxide and chlorine by means of a contact agent, preferably animal charcoal; platinum has also been used. It is now said to be made chiefly by the process of Michalske (U. S. Pat. 808,100 of December 26, 1905). In this process calcium chloride is heated with lime and coke breeze in an electric furnace; the carbonyl chloride is condensed as a liquid at 8° C. (about the freezing point of benzol). The carbonyl chloride gas is passed into the liquid dimethyl anilin at ordinary temperature until the weight increases 40 per cent; the mixture is then heated to

100° C. for several hours to complete the reaction; the product is a solid melting at 174° C.

By using grain alcohol in place of the wood alcohol, above, the corresponding ethyl product is obtained. It is not so important as the methyl product. "Ketone" is the nickname applied to the product made from dimethyl anilin, and "diketone" is that applied to the diethyl anilin product.

#### MAKING DYES FROM "KETONE"

In general, dyes are made from ketone by treating a mixture of it with phosphorus oxychloride or phosphorus trichloride with another coal-tar derivative; this operation is technically known as condensing. In Fig. III the dyes are represented by squares; the material combined with ketone to produce any one of these dyes is indicated on the oval next preceding the square.

Where phosphorus chlorides are used they are generally used in the proportion of 60 to 100 per cent of the ketone taken; toluol may also be used as a diluent when the amount of chloride can be reduced somewhat.

Many modifications have been introduced as to the condensing agent; zinc chloride, aluminum chlorid, and sulfuric acid may, in special cases, be used in place of the phosphorus chlorides. In general, the phosphorus compounds are the best condensing agents in this method. They appear finally as phosphoric or phosphorous acid. What is actually done with them is not

TABLE V—DATA ON DYES OF FIG. III

Schultz No. (1912)	THE TWENTY-FOUR DYES	Acid	Basic	Cotton mordanted	Wool	Chrome wool	Silk	Never patented	Expiration of patent	Parts from 100 parts ketone
	RED									
550(a)	Chrome bordeaux.....	x				x		x		150
	YELLOW									
493(b)	Auramine.....		x	x	x				1901	113
	GREEN									
509	Chrome green.....	x				x			1900	145
542	Agalma green.....	x			x		x		1925	237
564	Eric green.....	x			x		x		1916	201
566	Wool green S.....		x		x		x	x		160
	BLUE									
498	Turquoise blue.....		x	x			x	x		145
522	Victoria blue 4 R.....		x	x	x		x	x	1901	204
531	Eriocyanin A.....	x			x			x		272
538	Victoria blue R.....		x	x	x		x	x		170
539	Victoria blue B.....		x						1901	188
560	Night blue.....		x	x	x		x	x		184
562	Fast acid blue.....	x			x			x		177
563	New patent blue.....	x			x		x		1915	177
565	Acid blue S.....	x			x				1915	239
567	Chrome blue.....	x				x			1910	164
	VIOLET									
516	Crystal violet.....		x	x		x	x		1900	152
527	Acid violet 4 BN.....	x			x				1903	274
528	Fast acid violet 10 B.....	x			x			x		279
548	Acid violet 6 BN.....	x			x		x		1910	293
549	Chrome violet.....					x			1909	145
561	Acid violet 5 BNS.....	x			x				1915	180
518	Ethyl violet.....		x	x	x		x		1900	156
532	Alkali violet 6 B.....	x			x				1903	200
	TOTALS.....	15	9	7	17	5	11	8	11	4605

(a) Also calico printing.

(b) Also paper, leather, jute, cocoanut fiber, artificial silk and lakes.

definitely stated but their conversion into phosphorus chlorides seems feasible and obvious.

The course of materials in making ketone and condensing it may reasonably be represented as follows:

A—Carbonyl chloride (33.21) + dimethylanilin (90.31), yield ketone (100) + 100 per cent hydrochloric acid gas (21.24).

The figures in parentheses give the *theoretical proportions* for 100 parts of ketone; no account is here taken of losses.

B—Phosphorus oxychloride (100) + ketone (100) + intermediate material, yield phosphoric acid (11.87) + 100 per cent hydrochloric acid gas (13.25) + recoverable phosphorus oxychloride (81.47) + dye (x).

BY-PRODUCTS OF THESE 24 DYES—Therefore, in making 100 lbs. of ketone and making dye therefrom, 34.49 lbs. of 100 per

cent hydrochloric acid gas or roughly 100 lbs. of 33 per cent commercial muriatic acid are produced; of this only 30.51 per cent are usable in making the hydrochloric salts of such of the dyes made in this class as are basic; the remainder, or 70 lbs., of commercial muriatic is available for other purposes.

Table V gives relevant data as to the 24 dyes of the class here considered; of these only 9 are basic and in the case of all the other 15 the whole of the commercial muriatic producible is available for other purposes. Data as to the relative amounts produced of these 24 dyes are not available and any statement as to such relationship would have to be nothing but the baldest kind of guess.

#### THE CHEMICAL TRANSFORMATIONS

The manufacture of these 24 dyes calls for the following eleven chemical operations, each of which is briefly described below.

- |                |                   |                             |
|----------------|-------------------|-----------------------------|
| 1 Nitrating    | 5 Oxidizing       | 9 Condensing                |
| 2 Chlorinating | 6 Caustic-melting | 10 Carboxylating            |
| 3 Sulfonating  | 7 Alkylating      | 11 Diazotizing and coupling |
| 4 Reducing     | 8 Liming          |                             |

1—NITRATING—The material to be nitrated is treated with "mixed acid," *i. e.*, a mixture of nitric acid with sulfuric acid; generally only mono-nitration is effected; dinitrating and trinitrating are less frequently performed; the differences are wholly of proportions, times and temperatures. The kind or quality of nitration product is not in every respect under control but quite generally the reaction can be "steered" in the right direction. The spent mixed acid in many cases can be re-strengthened so that there is only a slight loss of sulfuric acid.

2—CHLORINATING—The material to be chlorinated is treated with dry chlorine gas (usually from the electrolytic caustic soda plant followed by liquefaction and gasification); as in nitrating there may be mono-, di- or tri-chlorinating and in addition the chlorination may be in the "ring" or in the "side chain," so, according to the material there may be six courses for the reaction to go; it is not so readily "steered" as is nitrating. In chlorinating, one-half of the chlorine employed appears as hydrochloric acid gas (100 per cent), so that for each pound of chlorine that is introduced one pound of 100 per cent hydrochloric acid is obtained, *i. e.*, 3 lbs. of commercial 33 per cent muriatic acid.

As an illustration of what this means, take Dr. Brunck's figures of 1900 wherein 4,400,000 lbs. of glacial acetic acid are chlorinated annually; these require not less than 5,200,000 lbs. of liquid chlorine and produce 3,900 tons of 33 per cent muriatic acid, or 11 tons daily. These figures are today, perhaps, doubled for the indigo industry alone. It is hardly to be expected that this amount of acid is thrown away.

Further, the above quantity of chlorine corresponds to about 5,850,000 lbs. or 2925 tons of caustic soda annually or 8.5 tons daily.

3—SULFONATING—The material to be sulfonated is treated with 98 per cent or with fuming acid, *i. e.*, oleum, according to the product desired. As a rule, the amount of sulfuric taken is several times that required to do the chemical work, the excess acting as a vehicle. Mono-, di- and tri-sulfonating may occur, and the course can be "steered" with difficulty except in a few cases. The excess sulfuric is as a general thing lost, either as calcium sulfate or as a weak and highly contaminated sulfuric acid of which a part only can be strengthened up; it is, as a rule, run into the sewer. In sulfonating, in general, much of the sulfuric doing chemical work is divided over a number of products and of these some are far less useful than others and the art of making both ends meet in this phase is dependent upon how fully these different sulfonation products can be used in dyestuff making.

4—REDUCING—As a rule, only nitro bodies (the products of nitration) are reduced; when reduced they yield amido bodies, *e. g.*, nitrobenzol yields amidobenzol, otherwise known as anilin. Reduction is, as a rule, effected by the use of iron in



the form of powder, filings, drillings, etc., with the aid of acetic or of hydrochloric acid. The iron residue is very largely reconverted into metallic iron. The world does not use enough iron salts to make even a dent in the amount of these residues available.

5—OXIDIZING—This is effected largely by means of lead peroxide; manganese dioxide and also permanganates are used; hydrochloric acid is generally used in connection with them although sulfuric acid is also used. The manganese residues are generally re-worked to peroxide while the lead residue is used for lead chromate and similar articles. Potassium bichromate (residue chrome alum) and chlorate of potash (residue chloride of potash) are also used for oxidation purposes.

6—CAUSTIC MELTING—The substance to be subjected to the caustic melt is, as a rule, a sulfonation product, and the purpose of this melt is to remove the sulfuric acid portion and put the hydroxyl group in its place. For example, benzol mono-sulfoacid yields hydroxy-benzol, *i. e.*, phenol or carbolic acid; naphthalene monosulfoacid yields alpha-naphthol or beta-naphthol, depending upon which particular monosulfoacid of naphthalene was used. The sulfuric portion re-appears as sulfite of soda. As a rule, the amount of caustic soda taken is greater than that required for the chemical work; the excess is lost as carbonate in weak water solution, carrying the sulfite; this is used for bisulfite production or Glauber's salt production, or is thrown into the sewer as commercial conditions may indicate.

This process is not easily "steered;" it calls for extreme care, and its success depends upon very minute details not always easily discoverable, and when discovered very conscientiously kept secret.

7—ALKYLATING—This is the introduction of methyl or ethyl groups into hydroxyl groups or into amido groups. Methylation is generally effected by the use of wood alcohol and hydrochloric acid under pressure in closed vessels at elevated temperatures; sometimes methyl chloride must be used. Ethylation is similar to methylation, using grain alcohol for the wood alcohol and ethyl chloride for the methyl chloride.

8—LIMING—This is generally applied to sulfonation products to separate the different chemical substances from each other; as a general rule the lime salt of one or more is soluble and of the other insoluble; lime or chalk may be used; generally lime is preferred on account of absence of frothing, but where that is not objectionable limestone or chalk is used. In this case all free sulfuric acid is rendered useless as sulfate of lime.

In another phase of liming, however, caustic lime is necessary, as in separating benzal chloride from benzo-trichloride; the former gives benzaldehyde which is blown off by steam and the latter gives benzoate of lime, which is further decomposed to give benzoic acid.

9—CONDENSING—This covers all those processes where two different substances (or two molecules of the same substance) unite to form a new compound by the loss or elimination of water or its equivalent between them; among the most common equivalents for water-loss is loss of hydrochloric acid or of ammonia.

Sulfuric acid is a common condensing agent and for this purpose is used in considerable excess; in general, it reappears as a very weak acid and is lost to the works; the other condensing agents such as chlorides of phosphorus and of sulfur, zinc chloride, aluminum chloride, antimony chloride and the like can, as a rule, be recovered in usable form and returned to the cycle at a slight additional cost.

10—CARBOXYLATING—This is generally performed by the action of an excess of caustic soda and pure carbon dioxide gas upon a hydroxylated, *i. e.*, phenolic or naphtholic substance; for example, phenol or carbolic acid yields salicylic acid and alpha-naphthol yields alpha-oxy-naphthoic acid. Salicylic acid has wide application in the coal-tar dyestuff art. The caustic is recoverable only as a salt (sulfate or chloride, etc.).

11—DIAZOTIZING AND COUPLING—An amido compound such as alpha-naphthylamine on treatment with nitrous acid yields a compound called diazonaphthalene; this operation is called diazotizing. When this result is brought into contact with salicylic acid in the presence of sodium carbonate or acetate it yields a new substance; this operation is called coupling. This product on reduction yields a new compound, amido-salicylic acid, and the original alpha-naphthylamine. The amido-salicylic acid is itself very useful in the coal-tar dyestuff art.

These two operations are the most ubiquitous and widely applied reactions in the entire industry; they serve to help in making intermediate products and to produce the multitudes of substances known as azo-dyes which make up more than 50 per cent of the individual dyes of the world's market. This group of azo-dyes is a terrific and bewildering maze of interlocked and interlaced substances and operations compared with which the 24 dyes here charted are the merest alphabet of simplicity, as is shown later under the benzidine dyes.

#### MAKING MICHLER'S KETONE

In making the ketone for the 24 dyes in Fig. III, four operations are employed:

Nitrating	Reducing	Alkylating	Condensing
The following twelve materials are needed:			
Benzol	Carbon monoxide		Sulfuric acid
Nitrobenzol	Chlorine		Iron filings
Anilin	Phosphorus		Muriatic acid
Wood alcohol	Nitric acid		Animal charcoal

The product of these operations and materials is *not* a dyestuff but must be *condensed* with other products; in fact we are now only ready to begin to make a dye but only *after* we have made several other substances—to be accurate 18 additional compounds to make these 24 dyes.

Table VI shows the distribution of operations and materials over the things other than "ketone" that are to be combined with "ketone" to make dyes.

For twelve of these 24 dyes *one* member of the four classes of organic materials, namely,

I = Fatty series    II = Benzol    III = Toluol    IV = Naphthalene

is sufficient; for the other twelve the following combinations of materials are necessary:

Classes	No. of dyes	Classes	No. of dyes
I and II.....	4	III and IV.....	1
II and III.....	1	I, II and III.....	3
II and IV.....	1	I, II and IV.....	2

The operations required are a total of 118. In Table VI "xx" indicates that the operation has to be performed twice in making one dye.

TABLE VI—MATERIALS AND OPERATIONS OF THE 24 DYES

Dye No.	Totals	I	II	III	IV	1	2	3	4	5	6	7	8	9	10	11	Totals
550.....	1		x						x	x						x	4
493(a).....	1															x	(a)
509.....	1		x					x	x	x							4
542.....	1		x			x	x	x	x								6
565.....	1			x				xx	x	x							5
566.....	1			x	x			x	x								5
498.....	1		x						x	x							3
522.....	3	x	x		x	xx		xx					x	x			6
531.....	3	x	x	x		x	x	x	xx	x							7
558.....	3	x	x		x	xx		xx									5
559.....	2		x		x	xx		xx									6
560.....	2		x	x	x			x	x				x	x			6
562.....	1				x	x		x	xx	x							6
563.....	1				x	x		x	xx	x							6
564.....	1				x			x	x								4
567.....	1				x			x	x	x							6
516.....	2	x	x			x											3
527.....	3	x	x	x		x	x										5
528.....	3	x	x	x		x	x	xx	x								7
548.....	2		x	x		xx		x	xx				x	x			8
549.....	1		x						x	x							3
561.....	3	x	x		x	x		x	x				x	x			6
518.....	2	x	x			x			x								3
532.....	2	x	x			x		x									4
TOTALS.....	41	9	14	7	11	21	5	13	31	12	5	8	8	11	3	1	118

(a) No. 493 (auramine) uses double chloride of zinc and ammonia only, in addition to "ketone."

## COAL-TAR PRODUCTS PARTICIPATION IN THE 24 DYES

In making the quantities of each of the 24 dyes given in Table V the material participation is as follows:

	Per cent
Ketone.....	52.11
Benzol.....	7.58
Toluol.....	5.21
Naphthalene.....	11.42
Phenol.....	1.69
Sulfonation, alkylation, etc.....	25.90
TOTAL.....	21.97
	99.98

Of the ketone 58.21 per cent are benzol so that the benzol participation in the 4605 parts of the above 24 dyes is a grand total of 37.91 per cent. That is, of the 4605 parts of these 24 dyes:

	Per cent	Per cent
Benzol.....	37.91	...
Toluol, makes up.....	5.21	...
Naphthalene.....	11.42	...
Phenol, makes up.....	1.69	...
TOTAL.....	56.23	
Ketone production makes up.....	21.80	
Sulfonation, alkylation, etc., make up.....	21.97	

It must not be forgotten that these 24 dyes are by no means made and sold in the proportions given in Table V. Therefore, in order intelligently to plan a works for these 24 dyes it must be known how these 24 individuals are to be distributed over the whole production in order to avoid waste of space, apparatus, material and time in laying out the relative position of buildings and their respective sizes.

## MAKING THE TWENTY-FOUR DYES

To carry out the 118 operations it is not intended to say that 118 sets of apparatus are necessary; the different sets of apparatus are 11 or a multiple thereof and how great that multiple is depends upon the relative amounts of each of the 24 dyes to be made and the time at which they must be manufactured. Further, one and the same apparatus is not necessarily adapted for any one operation on different compounds, *e. g.*, nitrating each of the three different materials to be nitrated, namely, benzol, toluol and naphthalene; nor will the same chlorinating apparatus do for all kinds of chlorinating, nor the same condensing apparatus for all condensations and so on through the list.

## UNIFORMITY OF PRODUCT

It must be borne in mind that Fig. III does not in any way attempt to show the different manufacturing operations and steps that are necessary to accomplish the indicated results; neither is it attempted to show on Fig. III the filtering operations, the precipitation operations, the blowings off with steam and other means of mere mechanical separation; between each and any two successive chemical alterations there are one or more mechanical operations not indicated, as well as secondary chemical changes such as the conversion of sulfo-acids into salts; bases into salts; the separation of the salts from their liquids and their purification, their drying, their storing. In addition to all this, of course, there is the large amount of testing that must be done at all stages of each operation and the exhaustive and careful test of each lot of final product before it is passed from one step to the other and of the finished dye before it is placed in the warehouse. The number of these operations is merely a matter of calculation and consideration but such a presentation would add nothing of moment for present purposes; on the contrary it would make Fig. III so complicated as to rob it of most, if not all, of its utility. Suffice it to say, that the tests are in many cases rapid and short but in other cases and particularly in the case of the finished products they are very refined, allow but a small margin for error or variation and require a great deal of care and painstaking in their execution. For example, in making beta-naphthol some alpha-naphthol is always formed and the users of beta-naphthol have become so refined in their requirements and demands that if a sample of beta-

naphthol carries more than  $\frac{1}{500}$  per cent of alpha-naphthol, that is, one part of alpha-naphthol in 50,000 parts of beta-naphthol, it stands a very good chance of being rejected. In making alpha-naphthol some beta is always formed and its presence in alpha is just as objectionable as is the presence of alpha in beta.

Therefore, not only are there a large number of operations, but these operations while not always under accurate control must, nevertheless, be carried out with great refinement and great exactitude and with great uniformity of final product in the majority of the cases; there are a number of cases where such refinement is not necessary but, needless to say, works that make only the rough goods could not hope to survive in competition with works that make both classes of goods. The buyers of dyestuffs, as a rule, subject the purchased goods to severe tests and even if they do not, the competition between the various makers of dyestuffs is so keen that they themselves have effectively and effectually raised the standard of the goods to be made.

That this industry is complex, interlaced and interlocked not only from the manufacturing point of view but the merchandizing viewpoint also must be clear from Fig. III which purports to present in the sketchiest of outline the inter-relationship of only  $\frac{1}{40}$  of the individuals of the industry.

## INTERLOCKING AND INTERLACING

In Fig. III there are several instances of the production of two or more things side by side in one and the same operation and all of these must be utilized somewhere in the works in order not to be a dead loss.

Take, for example, treatment of toluol with chlorine; three substances are unavoidably formed: benzyl chloride, benzal chloride and benzo trichloride in greater or lesser proportions. In Fig. III benzyl chloride is used in three dyes, benzotrichloride in one dye and benzal chloride in a group of dyes, itself much larger than this particular group of dyes; but each of these three compounds has uses in other dyes and groups of dyes. Merchandizing effort must be directed to keeping the products of all these three materials in alignment so that excess production of none takes place over market requirements. It is a much more complicated merchandizing operation than, for example, the alignment of the salt-cake and muriatic acid markets, and still it is easier in some respects because of the greater number of outlets available. Nevertheless, it is a task requiring great skill and much careful and painstaking attention.

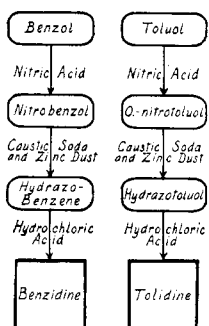
In treating toluol with nitric acid only one product is shown, namely, the para variety; however, another variety is also formed—the ortho variety which is commercially far more important than the para variety. In effect, therefore, the utilization of the para variety in this and other classes of dyes is merely making use of a substance unavoidably a by-product from another manufacture (*e. g.*, tolidine manufacture) so as to avoid useless waste and loss; if one maker does not the other will and thereby gain a commercial advantage. For example, the ortho variety is used in tolidine making and the para variety in magenta making (see Fig. VIII); both produce para and ortho respectively, in addition, which they respectively cannot use but *together* they can consume all of each *provided* their respective sales are properly adjusted; if not, additional uses are needed.

Other examples of such interlaced, interlocked simultaneous results are shown on Fig. VI; for example, the sulfonation products of beta-naphthol where one monosulfoacid and two disulfoacids must be kept in line; or the sulfonation of beta-mono-sulfoacid by means of oleum where at least two products, one disulfoacid and one trisulfoacid must be managed; direct loss of product with no use in this class is shown in the treatment of beta-monosulfoacid with nitric acid as described later on.

Study and examination of these charts or diagrams will dis-

close more and more how really intricate and complex as well as interdependent are these products. Nevertheless, simple inspection of these charts shows a real and important interlocking and interdependence of not only the intermediates but of the finished dyes themselves.

In Figs. IV, V and VI are presented the diagrams for 82 additional dyes and their needed intermediates; these 82 dyes are themselves important and large sellers. With the 24 ketone dyes just described they make up one-eighth of the individuals of the present world's market. The complex nature of the relationships of the relevant intermediates is obvious at a glance.



THE BENZIDINE DYES—FIG. IV

About one-tenth of the individual dyes on the world's markets have benzidine as a substantial and necessary ingredient. This can be made from nitrobenzol, caustic soda, zinc dust and hydrochloric acid and requires three chemical transformations, beginning with benzol as shown at Fig. IV. Benzidine itself,

however, is no dyestuff and, unlike anilin, it cannot be used for the production of black or any other shade upon fiber without the coöperation of some other coal-tar product. The benzidine must first be treated with nitrous acid to form its tetrazo-compound which is itself then combined with other coal-tar derivatives to produce finished dyes. In the production of the 82 benzidine dyes in the world's markets the materials or finished intermediates with which the benzidine is to be combined,

The original treatment of naphthalene, Fig. VI, is divided into three classes, namely, by nitric acid, by oil of vitriol and by fuming sulfuric acid. The nitric acid treatment followed by other suitable treatments yields 5 of these finished intermediates. The oil of vitriol treatment coupled with caustic melt, nitric acid treatment, reduction, treatment with nitrous acid and heating with water or with oil of vitriol yields 21 of these finished intermediate products; the treatment with the fuming acid yields but one finished intermediate.

When these 44 compounds are combined with benzidine to produce the 82 dyes, they are used two at a time, three at a time and four at a time or each one twice and it is self-evident from the possible permutations and combinations that there is a wide field opened up by these 44 finished intermediates; however, only 82 individuals have been found to be of lasting commercial value.

The benzidine dyes, which are valuable because they are direct cotton dyes (that is, dye cotton fiber without the use of a mordant), are incomplete of themselves for the commercial range of shades and colors in this class of materials and as a complement the tolidine dyes are employed. Tolidine is made from nitro-toluol (the ortho variety) in the same manner that benzidine is made from nitro-benzol (see Fig. IV). Tolidine, in turn, is combined with finished intermediates as is benzidine but requires finished intermediates over and above those shown on these charts and their genetic relationship is quite as complicated as that shown for the benzidine finished intermediates. Of the above compounds found in coal-tar only two are useful as such for union with benzidine and tolidine; they are phenol and cresol but the role they play in that capacity is rather subordinate.

The number of intermediate steps from naphthalene (Fig. VI) to finished intermediate is at a maximum in the case of 2.7

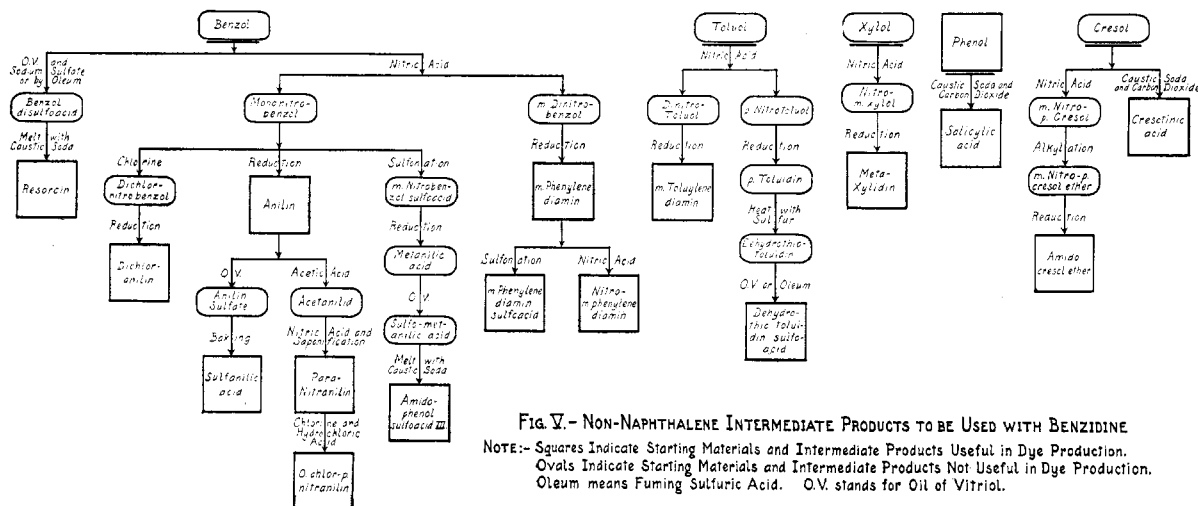


FIG. V.—NON-NAPHTHALENE INTERMEDIATE PRODUCTS TO BE USED WITH BENZIDINE

NOTE:—Squares Indicate Starting Materials and Intermediate Products Useful in Dye Production. Ovals Indicate Starting Materials and Intermediate Products Not Useful in Dye Production. Oleum means Fuming Sulfuric Acid. O.V. stands for Oil of Vitriol.

number 44. These 44 compounds are made from benzol, toluol, xylol, phenol, cresol and naphthalene and the making calls for the intermediate production of 55 substances that have, so far as these dyes are concerned, no other use than to serve as intermediate products.

Benzol, Fig. V, is treated with oil of vitriol or with nitric acid to form two different classes of benzol derivatives, the former having but one member and the latter having 9; toluol on treatment with nitric acid and three separate additional chemical treatments yields two finished intermediates. Xylol on treatment with nitric acid yields but one finished intermediate. Of course, other operations are necessary, such as the caustic soda melt, sulfonation, reduction, chlorination and baking. Phenol on carboxylation yields salicylic acid, and cresol on carboxylation yields cresotinic acid and on treatment with nitric acid and subsequently by alkylation and reduction yields amido cresol ether.

diamido naphthalene 3.6 disulfo acid; in that case six intermediate products must be prepared, no one of which has any use in this class of dyes, other than the production of this one finished intermediate. None of these starting materials yields a finished intermediate with one chemical operation except in the case of phenol and cresol; for all others at least two chemical steps must be taken before a finished intermediate is arrived at.

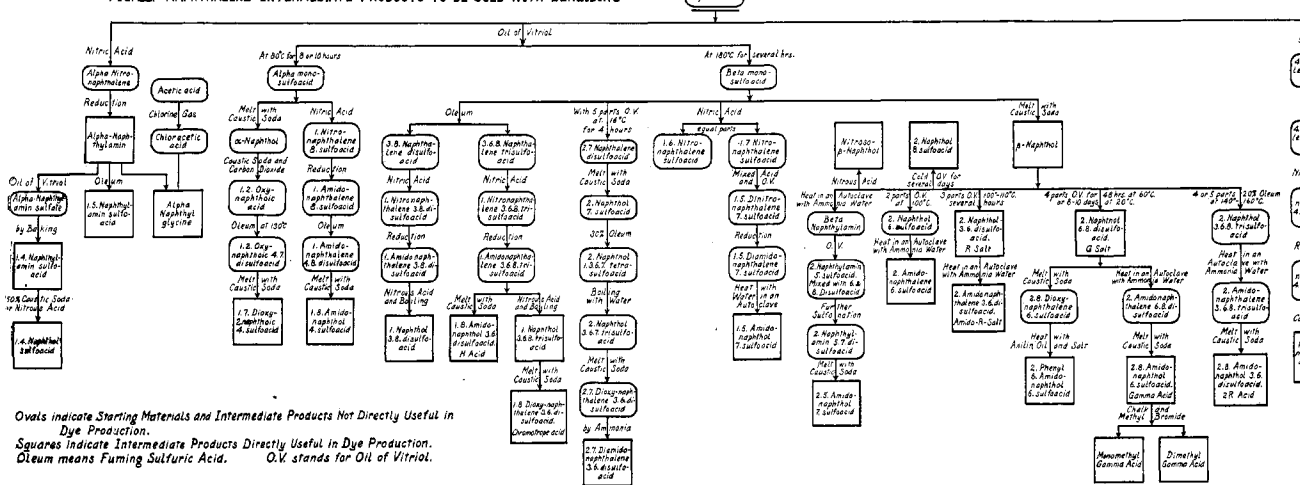
In addition to benzidine and to tolidine, 6 other substances of a similar nature are employed to complete this commercial series of direct cotton dyes and they in turn make use of some of these finished intermediates and in addition others not here charted.

Going back on Fig. VI, to the treatment of naphthalene beta-monosulfoacid with nitric acid it will be noted that the chart states that two nitration products are formed in equal parts; so far as this particular class of dyes is concerned one of those equal parts of nitration product is useless. It becomes a burden

to the other part so that the 1,5 di-amido naphthalene 7 sulfoacid must bear the entire cost of nitrating the beta-mono-sulfoacid although only one-half of that nitric acid and one-half of the beta-monosulfoacid is available for it; the other part

syntheses are divisible into 2 classes; three of them start from benzol and the remaining one starts from naphthalene and they all come together at the indoxyl point and from that point are all substantially identical. The salient point is at the pro-

FIG. VI.—NAPHTHALENE INTERMEDIATE PRODUCTS TO BE USED WITH BENZIDINE



goes to form a waste heap unless utilized in some other branch of the industry.

The 167 direct cotton dyes of the diphenyl type of the present world's markets are distributed as follows, among the various diphenyl derivatives:

Benzidine.....	82	Benzidine-mono-sulfoacid ...	2
Tolidine.....	43	Benzidine-di-sulfoacid .....	4
Dianisidine.....	28	Ethoxy-benzidine.....	4
o-Nitrobenzidine.....	1		
Di-chlorbenzidine.....	3	TOTAL.....	167

#### INDIGO

Four of the principal methods of making indigo have been charted (Fig. VII). In all processes of making indigo the chief difficulty has always been in getting a proper yield of indoxyl; the preparation of the glycine from which the indoxyl is made

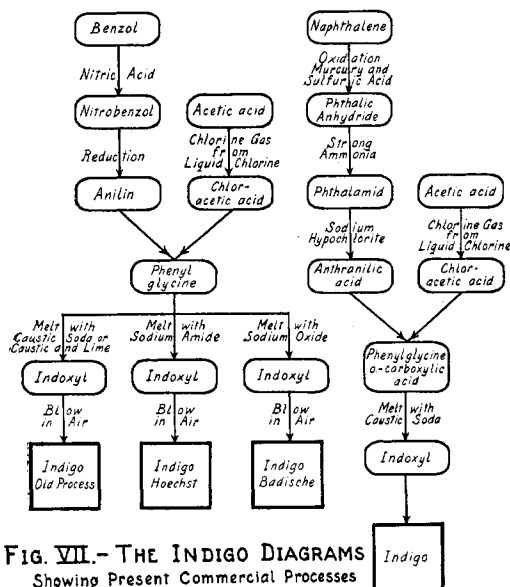


FIG. VII.—THE INDIGO DIAGRAMS Showing Present Commercial Processes

has in itself not offered any very great difficulty but the strategic point of the whole indigo synthesis is at that conversion, and it is at that point that most of the energy of chemists has been expended. It would not be at all surprising if on examination it were to turn out that at least 50 distinct and different modifications of operations at that point have been patented and of these probably not more than 3 survive to this day. These 4 indigo

duction of indoxyl. The method first to be used successfully commercially was to melt the glycine with caustic soda; when starting from anilin the yield rarely exceeded 45 per cent and for a long time no means was discovered for producing any substantial increase in that yield; admixture of burnt lime to the caustic soda was tried without materially increasing the yield. Moreover, all methods that started from benzol had to take account of the possibility of the drawback that to produce enough benzol to make the world's requirement of indigo would pile up such an amount of toluol that the industry simply could not use it and the indigo would have to bear the burden of the unused toluol. That is one of the primary reasons why the naphthalene method was the first to be used successfully commercially; further, the variety of glycine producible thereby was converted into indoxyl by melting with caustic alkali to an extent approaching 90 per cent of the theory; also the amount of naphthalene required to produce the world's consumption of indigo could be obtained without entailing the use of additional and other coal-tar hydrocarbons; i. e., there was plenty of naphthalene looking for a market and while there was enough benzol available, every time a certain additional amount of benzol was used, a certain amount of toluol was produced for which a market had to be created or be a burden to the indigo. However, in the last 15 years those conditions have changed; uses of toluol have been found and it is very likely that benzol will serve as the starting point for most of the world's indigo in the future.

However, it was not cheap benzol and it was not the finding of a use for toluol that made benzol feasible as a commercial starting point for indigo. The discovery that sodium amide would convert the glycine into indoxyl practically quantitatively was the particular event that made the use of benzol commercially feasible; sodium oxide has also been found to be a substitute of equally good quality for the sodium amide. Reverting to Fig. VII it will be of interest to note that the first step from naphthalene to phthalic anhydride today calls for the production of an amount of sulfuric anhydride equal to 80,000 tons of 50 per cent pyrites per annum. The step of passing from acetic acid to chlor-acetic acid today calls for over 9,000,000 pounds of glacial acetic acid and over 10,000,000 pounds of liquid chlorine.

#### AMERICAN ATTEMPTS TO DEVELOP A DYE INDUSTRY—FIG. VIII

The hydroquinone diagram in Fig. VIII illustrates what American manufacturers have been doing with domestic benzol; it requires a total of four chemical operations and produces two

compounds, each of them usable as such, *i. e.*, anilin, used for the production of black on cotton without the aid of any other coal-tar product and hydroquinone, used as a photographic developer. This diagram will give some measure of the difficulties that may be expected in an attempt to develop the finished intermediates necessary for the production of the 24 ketone dyes of Fig. III and the 82 benzidine dyes of Figs. V and VI.

Magenta requires benzol and toluol; the former must be converted into nitrobenzol and then into anilin and the latter into nitrotoluol (largely the para variety) and then reduced to toluidine by taking a suitable mixture of anilin and toluidine with nitrotoluol or nitrobenzol (as indicated in Fig. VIII), magenta base is produced, and this, on treatment with hydrochloric acid, yields the hydrochloride which is the commercial form of magenta.

A book of over 280 pages was published in 1889 and contained plates and drawings of apparatus and lay-out of works and minute directions for magenta manufacture; even this and the absence of all patents has not enabled American manufacturers to make this product in competition. It is true that magenta is still made in this country but it is made almost entirely from magenta base imported from abroad. Roughly and approximately speaking, in \$80,000 worth of magenta there are \$450 worth of commercial muriatic acid. The remainder of the value is made up by the magenta base.

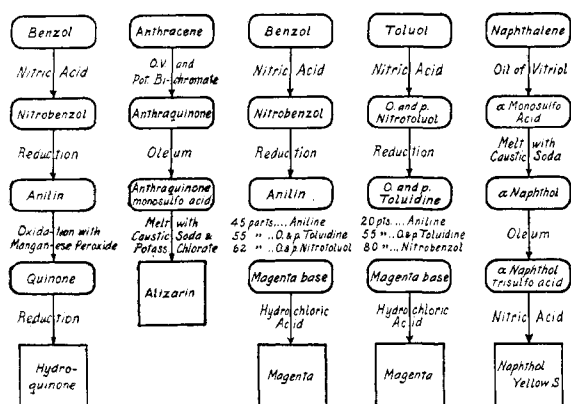


FIG. VIII.—SYNTHESIS OF SOME DYE-STUFFS ALL EXCEPT ALIZARINE ATTEMPTED IN THE UNITED STATES AND DRIVEN OUT BY FOREIGN COMPETITION

The Naphthol Yellow S patent has been dead for over 17 years and yet none of this dye has ever been successfully manufactured from naphthalene in this country. Whatever has been manufactured in this country has been made from alpha-naphthol-trisulfoacid, imported from abroad, which is merely treated here with nitric acid and carbonate of soda and even that manufacture has now disappeared almost entirely.

Alizarin manufacture involves three chemical transformations of anthracene which has always been as cheaply laid down from England in the United States as in Germany; the reputation of alizarin as a money-maker and money-getter has always been world-wide, and the United States has always been a good consumer of alizarin, yet no concern in this country has ever taken up the manufacture of alizarin. It is possible that the fact that alizarin never was protected by tariff may have prevented any such effort; certainly with the patent dead for 28 years it cannot well be urged that patent rights have stood in the way.

Many of the other dyes said to be made in the United States are made in just about the same way as the Magenta and Naphthol Yellow S; that is, the bulk of the chemical work is carried out in Germany and merely the finishing touches (the "as-

sembling") is done in this country. Obviously the bulk of the profit is not in the "assembling."

#### WORKING CLAUSES

These two examples show very clearly how a working clause in the patent law does not necessarily produce a coal-tar dye industry. The patent is taken out on the commercial form and any product prior to the commercial form is *not* the subject of the patent. It requires no lengthy dissertation to show that merely putting on the finishing touches is a long way from a true industry. France has had a working clause for a great many years, Great Britain for only seven, yet neither country today can make its dyestuffs simply because they have both been purchasing from Germany materials which bear the same relationship to the finished product that magenta base bears to commercial magenta and alpha-naphthol-trisulfoacid bears to Naphthol Yellow S. A true industry requires making all materials from the crudes.

#### GEOGRAPHY OF THE GERMAN DYE FACTORIES

In Germany the coal-tar dye plants and the principal coke oven districts are all contained within an area described by a square 300 miles on each side (see map). With but one exception the really important ones are all along the Rhine or a short distance up its tributaries. This whole district could be put inside the State of Wyoming, is much smaller than the state of New Mexico, or is smaller than New York and Pennsylvania combined. With cheap water routes and short rail hauls for the transportation of materials from one factory to another or to sea port, these dyestuff factories are most advantageously located and with the added short rail and water hauls to them from the coke regions the transportation of the raw materials to the dyestuff works is economically profitable.

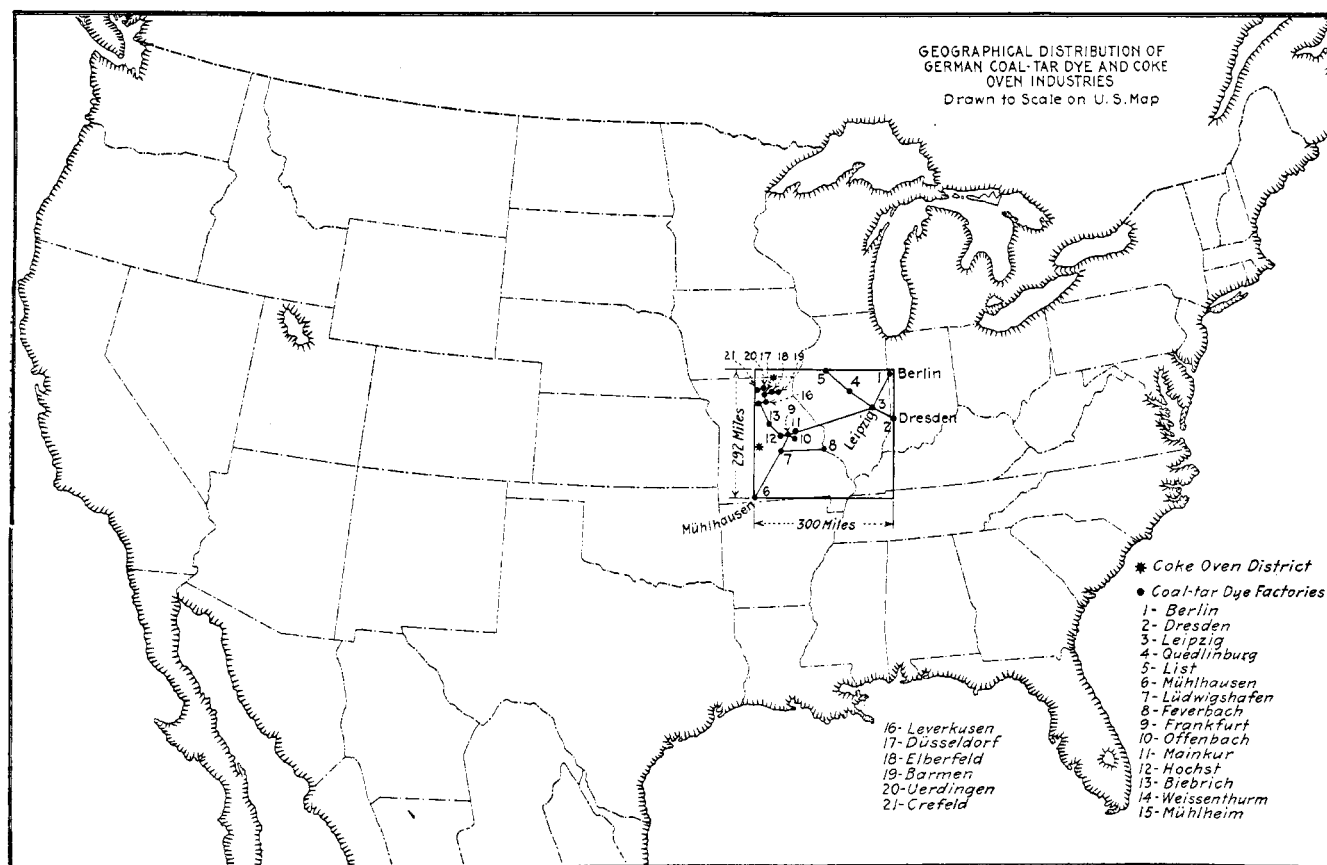
#### WHY GERMANY CONTROLS THE COAL-TAR DYE BUSINESS

The average annual unit gross per year of the 900 coal-tar dyes, exclusive of alizarin and indigo, all over the world outside of Germany, has previously been shown to be about \$41,000. Add to this the interlocked dependence of intermediates and finished dyes just shown and the facts that the German works have long ago fully paid for their plants, their experience and their sales organization and the result is what seems to be a complete answer to why Germany controls the world's coal-tar dye market. In fact, the whole industry, taking everything into account, is just about a one-nation business. It is a business made up of a large number of small units with all units essential to success.

Germany has this business established in 33 other countries; it is evident that any country starting in now would be greatly handicapped thereby if it attempted to enter the race for the full distance.

Although Germany has relied upon Great Britain for its crudes, *i. e.*, its benzol, its toluol, its naphthalene and its anthracene, up to the middle of the 90's and perhaps later, England has not been able to make any headway as competitors in dye manufacture, but on the contrary has lost ground. Many of these non-patented world's dyes are also non-patented in England yet most of Great Britain's requirements of those materials have always been supplied by Germany.

The answer to the question as to why Great Britain has not succeeded against Germany cannot be that Great Britain is not a nation with highly developed chemical industries. A German chemist as well equipped as any other living man to express an opinion and to compare German industries with British industries has said the following: "To be sure, we know that several of the European countries, *e. g.*, England, are still ahead of us in many branches of the chemical industry, especially in inorganic manufacture. But in no country on earth are those branches of the chemical industry which demand versatility of thought, and particularly a large body of scientifically trained employees, so well developed as with us. Our



synthetic dye, synthetic drug, and perfumery industries are foremost throughout the world, and there is probably no country in which the heads of factories are so imbued with the conviction that their employees must needs cast a glance beyond domestic boundaries."

Each one of the large chemical manufacturing countries of Europe, without exception, buys more intermediate products from Germany than it sells to Germany and all of the countries but one, namely, Switzerland, buy more dyestuffs from Germany than they sell to Germany. In other words, and broadly speaking, all the rest of the world, outside of Germany, merely assembles intermediates purchased from Germany, into finished dyes; Germany alone makes all its own intermediates; that is, Germany makes all the dye-parts and the rest of the world merely assembles these dye-parts into finished dyes. Needless to say, the one who controls the manufacture of dye-parts actually controls the manufacture of dyes.

Where Austria, Belgium, France, Great Britain, Italy, Russia and Switzerland singly and combined have failed, in spite of their other large chemical industries, to take away this business from Germany, the American chemist should not be blamed nor found fault with because he has not succeeded, nor should it be assumed that transplanting of the whole industry can be done at once and is a perfectly easy thing to do, as so many seem to think. The transplanting of that industry out of Germany is an undertaking properly and fitly to be described as titanic.

Why the other countries have failed is probably due to the fact that they contributed little or nothing to the real upbuilding of the business, and to its creation, for the coal-tar dye business is a *created* business; those who aided in its creation were first in the position to reap the benefits—an advantage they have no doubt earned and deserved through the effort they expended and the risks they assumed.

#### GERMANY AND THE UNITED STATES

In 1913 Germany had for sale to foreigners \$3 worth of these products as against every dollar's worth that it needed at home; the total coal tar dye imports of the U. S. constitute less than 0.4 per cent of our entire import business.

Nine hundred different dyes were on the United States markets of which 100 were made or assembled in this country from intermediates purchased from Germany. Yet these 100 do not seem to be enough for American dye-users.

How much less than the full 900 will satisfy American users is known to them and to the importers. The latter cannot be expected to divulge that information; if the former want substantial help from American chemical makers *they* must divulge that information; no other way of ascertaining it is available.

In 1909 the United States produced \$3,462,436 worth of artificial dyes which are probably anilin dyes in the strict sense. Compared with Switzerland's \$3,200,000 production, *i. e.*, "assembly," in 1896 this is an achievement of which Americans need not be ashamed. The wonder is not that we have not done more but that in the face of the well organized manufacturing plants of Germany and of Germany's very much superior facilities for foreign trade, both banking and carrying, that we have done as much as we have. Blame should not be parcelled out for what American chemists have not done, but credit, which has been withheld so far, should be given for what has been done in spite of obstacles abroad and obstacles at home. The users of dyestuffs have invariably opposed any tariff enactment that would substantially encourage a domestic production of coal-tar dyes. That so many are produced in this country as are being produced is due to no coöperation of dyestuff users but has been accomplished in spite of their obstruction and if today the users are in serious difficulty through a lack of dyestuffs they have their own shortsightedness to blame and cannot, by any argumentation whatever, shift the blame to American chemists.

With proper help and encouragement the American chemist will be able to increase the domestic production of coal tar dyes and to inaugurate the making of intermediates; in the course of time this country may then ultimately look forward to a substantial share of the world's coal-tar dye business.

Hardly any of the valuable or useful intermediates ever were patented. A considerable number of non-German chemists have invented and patented finished dyes made from non-patented intermediates. These inventors had perfect freedom to make the needful intermediates and an *exclusive* right to make, sell and use their new dyes therefrom, yet they bought their intermediates from Germany rather than make them themselves. The patent situation is, therefore, really, that Germany excelled the rest of the world in making patentable combinations from non-patented and non-patentable intermediates and further in making those intermediates in open competition with the rest of the world. So, from one point of view, it appears that the rest of the world, inclusive of the United States, lay back, let the Germans do all the hard work and when the rest of the world finally woke up to the value of what the Germans had accomplished they became very busy making excuses and explaining instead of making a determined, directed, united and effective attempt to recover the ground so lost. That such recovery will require the hardest kind of work on the part of all—users, capitalists, consumers and makers alike—is self-evident and obvious and the question is: Do we want to pay the price? It can be done, if the price be paid.

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### GAS MANUFACTURE FROM THE POINT OF VIEW OF PHYSICAL CHEMISTRY<sup>1</sup>

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In past practice, gas manufacture has been primarily an engineering problem, with the chemist a more or less necessary adjunct for the analysis of coal, coke, oxide, etc. The research chemist, who deals with the processes of manufacture and the phenomena of reactions involved, has been looked upon as a burden unwarranted by returns. In view of the present available raw materials for gas manufacture on the one hand, and the demands of the public on the other, the advisability of continuing the policy of the past becomes a serious question.

There are few industrial operations which, from the standpoint of physical chemistry, are more complex in their nature than the treatment by heat of coal, oil and water in the production of coke, gas, tar, ammonia and cyanogen. In gas manufacture practically all the variables of chemical phenomena are involved. While this fact greatly complicates such industrial problems theoretically and practically, at the same time it greatly enlarges their possibilities; it strongly emphasizes the need of continued scientific research and investigation in connection with them. The heat treatment of coal, oil and water necessitates dealing with the chemical reactions of solids, liquids and gases, and with all the laws, both physical and chemical, which govern these reactions. The finest equipment in the world, designed with utmost mechanical precision, but without regard for the laws which govern the reactions carried out in it, is likely to be less useful than apparatus of the most wretched mechanical construction, but which does consider the chemical changes involved. Obviously, the aim of any industrial operation is perfection, both of process and apparatus.

Problems that are primarily chemical, and which can be attacked most efficiently from a chemical point of view, are common enough in gas manufacture. Who of the gas men present have not, at some time or another, faced the problems resulting from naphthalene, drip oil, fluctuating candle power, deposited carbon, ammonia, sulfur, cyanogen, or any one of a dozen other

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factors? Further, every new development in gas manufacture will create new problems. Every improvement will involve some question or questions peculiar to it. The greater the number of researches, the greater is the progress in a given field, and the greater becomes the number of new problems.

Hitherto, the greatest progress in American gas manufacture has been made along mechanical lines, and, as Americans, we may be proud of this progress. Chemical development, however, has been far behind the mechanical and operative improvements. It may be said that we have been spending too much of our energy investigating the machine rather than what is going on inside of the machine. Were the machine the end product of vital importance, improvements of this character would be unquestionable but the gas factory of the future will earn, or fail to earn, its dividends as it turns out, or fails to turn out, the best relative yields of coke, gas, tar and ammonia. It is true that the machine and the process are vitally related; there may be objections to this point because engineers are constantly working to perfect processes. It seems in gas manufacture, however, that too many of the purely theoretical chemical problems have been left to the mechanical or erecting engineer for solution. A mechanical, electrical or civil engineer, whose primary profession is the building and operation of machines and equipment, whose academic training consisted in the study of chemistry and physics during a part of two years, should not be expected to be as efficient in chemical research as the man who devoted himself exclusively to the study of chemical and physical phenomena; it is the latter, furthermore, whose primary profession to-day is the study of chemical and physical phenomena. To carry out high-grade research and investigation in any line, well-paid specialists must be employed. The able and efficient chemist and chemical engineer can do better things than analyze coal and iron oxide, however efficient he may be at the latter.

The day is past when gas-making is primarily a mechanical operation. Carbureted water gas constitutes approximately two-thirds of the gas made to-day, and it is no longer possible to buy a high-grade paraffin gas oil for 3 cents a gallon. Consequently, the petroleum supply becomes a most vital and important problem to the American gas manufacturer to-day. The importance of the oil problem as related to gas manufacture can be conveyed by the fact that in 1913 Greater New York alone used approximately 3,860,000 barrels of oil in the manufacture of carbureted water gas.<sup>1</sup> During 1913 the same plants used approximately 1,600,000 tons of coal. On the basis of heat units involved, oil has become as important in American gas manufacture as coal. Furthermore, Greater New York constitutes but one center for gas manufacture. I need not elaborate on the importance and seriousness of this oil problem, because you are fully acquainted with it. During the last decade, the increasing price of oil for gas manufacture has created what many gas men regard as a "dangerous" situation; and this is true despite the fact that never before in the history of the United States has so much oil been produced as to-day.

Why is it, then, that gas oil is expensive? Why should hundreds of millions of dollars' worth of oil-carbureting machinery be threatened? What is it that makes the economical use of petroleum one of the chief problems of the gas manufacturer? It is, first, the scientific progress in petroleum refining, and, second, the changing character in composition of the oil from newly discovered fields. Through careful scientific investigation, and through the application of physical-chemical principles, pure and simple, the refiner has perfected processes whereby the oil which you used to buy at 3 cents a gallon is now converted into gasoline and other end products which sell at several times that price. A representative example of this progress can be

<sup>1</sup> *Gas World*, 61 (1914), 76.