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MARKETING MINERAL PIGMENTS[1/]

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CONTENTS

GENERAL DEFINITION AND USES

A mineral pigment is a colored substance dug from the ground, which after treatment can be mixed with a drying oil to form a paint. Not all colored earths, however, can be made into satisfactory pigment. Much depends upon the attractiveness and uniformity of the color and the ease of purification. Mineral pigments are distinguished from chemical pigments by a difference in origin and treatment. Chemical pigments are not found ready-made in the earth but must be synthesized or otherwise obtained from other compounds or elements; as for example cadmium yellow, a chemical pigment, is precipitated from a solution of cadmium chloride, hydrochloric acid, and sodium sulfide.

1/ This paper is a slightly revised form of Information Circular 7198, Marketing Natural Mineral Pigments, issued in February 1942. The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7217."

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The American war program has increased the importance of mineral pigments. The Army uses a great deal of ocher and chromic oxide in camouflaging material to match landscape and consumes many thousands of gallons of olive-drab mineral paint in the impregnation of canvas, which is dipped in the paint, squeezed through rollers, and festooned to dry. The United States Navy is a large user of Spanish reds for ship-bottom paints and Venetian reds in porous antifouling compounds. In Great Britain the camouflaging of many acres of factory roofs has opened a market for cheap, coarsely ground mineral pigments and fillers such as slate, quartz, and off-color ochers, which normally are unsalable. Both Allied and Axis powers have resorted to the alteration of landmarks near vital military points to deceive enemy bombing squadrons, and inexpensive mineral pigments have been applied wholesale in carrying out these ruses.

In addition to wartime uses, mineral pigments are employed in private industry to give color, opacity, or body to paint, stucco, plaster, mortar, cement, linoleum, oilcloth, rubber, and sundry plastic materials. The borderline between pigments and fillers or extenders is not always clear; however, uncolored clays, barite, whiting, etc., are not usually classed as "pigments," probably because they have so much less opacity or hiding power than the manufactured white pigments, such as white lead, zinc oxide, lithopone, or titanium white.

Mineral pigments find their main outlet in low-priced paints, both alone and mixed with chemical pigments. Iron oxide pigments are used extensively in the preparation of paints for the protection of iron and steel work from rust, competing with graphite and red lead for this purpose. Iron oxide paints are also used on freight cars, barns, etc. Other uses for iron oxide pigments are as coloring agents and fillers in the manufacture of imitation leather, shade cloth, shingle stain, and paper and cardboard filler. Siennas and umbers are used in wood stains and wood fillers. Comparatively large amounts of ground sienna were formerly used for lithographic and typographic printing, but this use is now negligible. Some sienna is used as an artists' color. A considerable quantity of umber is consumed in the wallpaper industry and in furniture paints and stains. Ocher, in addition to its use in paints, is also used as a pigment (toned up with dyes) for linoleum and oilcloth, as a pigment in wood stains and wood fillers, and in coloring cement, stuccos, and mortars. Graphite paints are used for the protection of bridges, railroad cars, smokestacks, boiler fronts, tanks, metal roofs, and other exposed surfaces.

The mineral pigments are more fully described on pages 15 to 17.

In the nineteen twenties there were 35,000 to 40,000 tons of mineral pigments used in mortar colors annually, but this use has now declined to perhaps 10 percent of its former volume. Consumption of mineral pigments in linoleum is probably of comparable volume.

During the past 10 years the standards of the American pigment industry have grown to be the best in the world, and most of the foreign pigments formerly imported because of fair quality and low freight have failed to keep pace with the advancing standards of the American pigment processers. The curtailment of imports of French yellow ochers, Spanish red oxide, Persian Gulf red oxide, Turkey umbers, and Italian siennas during World War II is therefore not the hardship which it might appear.

SURVEY OF THE PAINT INDUSTRY

As mineral pigments are used chiefly in paints, a general outline of the paint industry may indicate the factors that influence production of and demand and markets for pigments.

The use of mineral pigments in paint goes back to the art of prehistoric cave dwellers. For example, in 1879 the Marquis de Sautuola while exploring a cave in northern Spain discovered a beautiful painting of a bull on its wall. The pigments in this instance were found to consist of a red sienna, a deep blue containing an oxide of manganese, and a variety of yellows and oranges composed of iron oxides and carbonates. The colors had been mixed with animal fat to make them stick to the cave wall. Many similar archeological discoveries have since been made.

Many of the pigments used in the modern paint industry were known at the beginning of the Christian era. The manufacture of white lead (basic carbonate of lead) from metallic lead and vinegar was described by Pliny. Zinc oxide was obtained by roasting zinc ores with charcoal and was known as "philosopher's wool."

Linseed-oil paints were used probably as early as the sixth century A.D., and were rediscovered in about 1400 by the Van Eycks, two Flemish artists of the Renaissance. Before the end of the eighteenth century linseed-oil paints were considered quite important in Europe but less so in the United States. The ordinary colonial house was whitewashed, oil paints being reserved for dwellings of the more prosperous citizens and for public buildings.

There were American importers of pigments as early as 1772, and in 1804 one of these erected the first white-lead factory in the United States in Philadelphia.

No doubt paints in smaller quantities had been manufactured or mixed locally during this period as the need arose. A New England curiosity is a stone ball (known as the Boston Paint Stone) resting on a stock block - a colonial device for grinding pigments with linseed oil.

In 1857 the first paints in cans - ready-mixed paints - appeared. Despite opposition of painters who were accustomed to mixing their pigments and linseed oil personally, the sales of canned paint increased and today represent the bulk of domestic paint sales.

The value of paints produced in the United States and the number of paint factories have increased fairly steadily, except during the postwar period and during the depression of the early nineteen-thirties. Bureau of the Census statistics, which include pigments, prepared paints, varnishes, and other paint products for specified years since 1899 are given below:

Year	Value of production	Number of factories
1899	$ 69,562,235	600
1904	90,839,609	639
1909	124,889,422	791
1914	145,623,691	800
1919	340,346,803	830
1921	274,310,314	804
1923	404,134,231	826
1925	470,736,264	923
1927	519,009,842	1,006
1929	568,975,838	1,063
1931	350,725,652	1,039
1933	289,441,956	961
1935	416,999,506	1,082
1937	538,460,629	1,124
1939	434,938,754	1,165

Most of the plants are situated in the North Atlantic States, the Great Lakes region, and on the West coast. In 1937 New York State had 161 establishments producing paints; New Jersey, 126; California, 115; Illinois, 107; and Ohio and Pennsylvania, 97 each.

As natural mineral pigments are produced principally in Georgia, Virginia, Pennsylvania, and other Atlantic Seaboard States, most producers can ship cheaply via rail and water to nearby consuming points in the East.

The number of employees in American paint plants is small in comparison with the number of persons who derive income from paint in other ways. It is of interest to note from the following data (supplied by the Bureau of the Census) the wide variation in number of painters, glaziers, varnishers, and enamelers employed as compared with the number of employees in paint factories.

Wage earners in paint factories		Painters, glaziers, varnishers, and enamelers	
Year	Number	Year	Number
-	-	1860	54,339
-	-	1870	85,657
-	-	1880	128,556
1899	9,697	1900	277,541
1904	11,633	-	-
1909	14,240	1910	337,355
1914	16,083	-	-
1919	21,507	1920	323,032
1921	18,015	-	-
1923	22,818		-
1925	25,490		-
1927	28,061	-	-
1929	29,211	1930	528,931
1931	22,521	-	-
1933	22,880	-	-
1935	27,686	-	
1937	31,664	-	-
1939	28,237		

Although figures showing consumption of paints in the United States are not compiled, the Bureau of the Census has gathered data covering domestic sales of paints by a specified number (680) of American paint producers as follows:

Year	Value
1928	$420,514,471
1929	434,817,446
1930	348,152,692
1931	278,255,312
1932	202,920,599
1933	220,303,893
1934	276,206,117
1935	334,277,609
1936	398,032,770
1937	419,103,821
1938	347,382,114
1939	394,508,431
1940	396,622,786

The figures do not give total United States sales of paint, but only the sales of the same 680 firms year by year. The table merely shows the trend in sales.

FOREIGN TRADE IN PAINTS AND PIGMENTS

In addition to pigments, American manufacturers produce virtually every known variety of paint, varnish, and lacquer. American paints and pigments are found in nearly every world market and have maintained their general position despite the growth of domestic paint industries in former markets, particularly in certain Latin American countries. American specialty paints, including high-quality lacquers, have frequently been preferred to similar European materials. Before the outbreak of World War II pigments and paint raw materials were purchased in many markets upon a price basis only, and American materials suffered in competition with inferior but cheaper German and Japanese products. Most South American importers, although interested in American products as temporary replacements, may return to the cheaper German brands when they can get them again. The lack of dollar exchange has hindered South American purchases of American paint products to some extent in the past, but trade agreements negotiated by the United States with several of the Latin American republics in 1941 may relieve this situation. Sea warfare, occupation of former American markets by Axis forces, and shortages of bottoms may curtail total overseas paint shipments for the duration of the war.

The following table indicates the value of pigments, paints, varnishes, and lacquers shipped from the United States by years from 1900 to 1940.

United States Exports of All Types of Paints[1/]

Year	Value	Year	Value
1900	$ 1,902,367	1921	$ 12,132,850
1901	2,036,343	1922	11,479,260
1902	2,096,379	1923	16,551,725
1903	2,350,937	1924	14,326,200
1904	2,756,581	1925	18,510,021
1905	3,126,317	1926	18,887,627
1906	3,773,064	1927	20,098,455
1907	3,931,899	1928	25,613,621
1908	4,001,824	1929	29,111,492
1909	3,959,080	1930	21,689,217
1910	4,726,565	1931	15,126,896
1911	6,294,746	1932	10,365,626
1912	7,072,617	1933	11,835,199

See footnotes p. 7.

United States Exports of All Types of Paints[1/] (Cont'd.)

Year	Value	Year	Value
1913	$ 7,681,938	1934	$ 14,206,848
1914	7,274,318	1935	16,343,667
1915	7,415,723	1936	17,788,597
1916	11,416,329	1937	21,555,034
1917	15,041,500	1938	18,654,718
1918	17,511,611	1939	22,761,510
1919	25,508,426	1940	2/ 22,433,561
1920	28,600,608		

1/ Data obtained from Foreign Commerce and Navigation of the United States, Bureau of Foreign and Domestic Commerce.

2/ Preliminary figure.

A tabulation of exports of all varieties of paints, by countries of destination, for even a single year would require much space, but the extent of foreign consumption of American finished paints is indicated sufficiently by the exports of the three principal items to their respective major markets during 1939, compiled by the Bureau of Foreign and Domestic Commerce as follows:

Exports of ready-mixed paints, stains, and enamels from the United States in 1939

Country	Gallons	Value
Philippine Islands	368,356	$ 518,064
Venezuela	193,157	325,840
Colombia	185,001	356,178
Mexico	119,700	232,375
Netherlands West Indies	118,440	219,553
Argentina	114,120	200,816
Canada	104,084	177,003
Brazil	103,347	200,029
Other countries	1,301,147	2,477,437
Total	2,607,352	4,707,295

Exports of nitrocellulose lacquers, pigmented, from the United States in 1939

Country	Gallons	Value
Union of South Africa	105,522	$ 228,737
Sweden	61,970	142,384
Brazil	58,690	142,526
Argentina	58,072	134,207
Mexico	42,276	86,996
Belgium	39,038	77,265
British India	23,346	47,385
Canada	21,740	52,836
Other countries	190,457	452,264
Total	601,111	1,364,600

Exports of paste and semipaste paints from the United States in 1939

Country	Pounds	Value
Panama Canal Zone	499,744	$ 48,935
Philippine Islands	421,355	40,430
Canada	365,444	81,929
Venezuela	144,554	16,930
Cuba	136,341	22,980
Union of South Africa	128,097	17,328
Brazil	120,261	21,953
Argentina	92,570	23,390
Other countries	1,359,514	249,598
Total	3,267,880	523,473

The exports, by total quantity and value of all products classified in the paint and pigment export schedule, follow for 1939:

(Source: Bureau of Foreign and Domestic Commerce)

Item	Quantity	Value
Ocher, umber, sienna, and other forms of iron oxide for paints .... lb.	10,910,436	$ 299,289
Other mineral earth pigments .... do.	41,048,145	516,337
Zinc oxide .... do.	6,970,249	532,670
Lithopone .... do.	9,690,621	392,798
Lampblack .... do.	957,587	81,956
Carbon black or gas black .... do.	203,827,817	8,888,666
Red lead .... do.	2,647,536	186,396
Litharge .... do.	4,155,287	253,731
White lead, dry .... do.	2,933,057	180,479
White lead in oil .... do.	1,114,341	94,832
Titanium dioxide and titanium pigments.... do.	8,638,565	698,063
Other chemical pigments .... do.	9,947,242	1,493,424
Bituminous paints, liquid and plastic	-	384,157
Paste and semipaste paint colors in oil, putty and paste wood filler .... lb.	3,267,800	523,473
Kalsomine or cold water paints, dry .... do.	9,225,205	491,135
Nitrocellulose (pyroxylin) lacquers, pigmented .... gal.	601,111	1,364,600
Nitrocellulose (pyroxylin) lacquers, clear, do.	246,865	480,725
Thinners for nitrocellulose lacquers do.	796,173	554,370
Ready-mixed paints, stains, and enamels, do.	2,607,352	4,707,295
Varnish .... do.	447,207	637,114
Total		22,761,510

Imports of mineral pigments into the United States for consumption[1]

Year	Iron-oxide pigments, natural and synthetic		Ochers and siennas		Other		Total value
	Pounds	Value	Pounds	Value	Pounds	Value	
1900[2]	(3/)		10,733,026	$ 88,139	(4/)	$163,810	$ 251,949
1901			8,206,925	70,125		145,420	215,545
1902			10,921,864	131,772		168,723	300,495
1903			12,642,271	143,168		342,659	485,827
1904			10,653,867	116,040		202,822	318,862
1905			11,702,403	115,237		208,903	324,140
1906			11,654,823	118,766		140,625	259,391
1907			14,209,074	142,323		195,427	337,750
1908			12,221,380	113,021		279,726	392,747
1909			13,377,414	122,491		191,303	313,794
1910			18,330,565	167,761		200,356	368,117
1911			16,370,268	164,580		219,270	383,850
1912			14,520,532	147,413		223,265	370,678
1913			21,562,861	220,715		284,699	505,414
1914			22,153,168	163,128		370,034	533,162
1915			24,086,259	189,217		257,339	446,556
1916			23,255,667	138,504		303,689	442,193
1917			20,864,081	274,435		385,746	660,181
1918			9,963,106	253,801		356,363	610,164
1919			10,877,984	265,939	14,311,006	350,340	616,279
1920			35,019,568	521,152	23,799,927	746,123	1,267,275
1921			11,668,505	256,628	24,610,815	604,242	860,870
1922			5,350,906	97,956	19,108,814	255,532	353,488
1923			21,022,483	343,938	78,659,740	994,760	1,338,698
1924			19,657,287	249,689	76,662,149	835,218	1,084,907
1925			20,138,814	275,020	82,591,011	934,821	1,209,841
1926	27,987,043	$666,843	20,845,696	390,151	(4/)	480,783	1,537,777
1927	24,050,327	587,634	20,872,369	448,494		594,372	1,630,500
1928	25,491,489	607,352	21,499,263	432,941		507,824	1,548,117
1929	24,440,925	599,157	22,033,745	416,361		600,837	1,616,355

See footnotes p. 11.

Imports of mineral pigments into the United States for consumption[1] (Cont'd.)

Year	Iron-oxide pigments natural and synthetic		Ochers and siennas		Other		Total value
	Pounds	Value	Pounds	Value	Pounds	Value	
1930	17,038,482	$375,176	14,576,024	$273,567		$368,304	$1,017,047
1931	12,086,887	255,348	11,994,803	190,813		420,013	866,174
1932	9,708,913	171,419	7,728,348	108,087		237,762	517,268
1933	13,202,467	257,137	11,147,022	170,773		322,106	750,016
1934	13,451,547	291,984	9,185,359	179,681		260,976	732,641
1935	19,888,511	542,243	12,631,097	254,262		372,465	1,168,970
1936	15,675,139	414,488	10,219,728	141,007		314,717	870,212
1937	16,791,602	492,728	13,084,230	216,154		519,322	1,228,204
1938	10,043,546	323,703	6,674,115	104,586		265,062	693,351
1939	16,913,722	477,134	9,703,804	157,660		214,119	848,913
1940	19,329,418	495,188	5,828,450	91,997		132,664	719,849

1/ Source: Foreign Commerce and Navigation of the United States, Bureau of Foreign and Domestic Commerce.

2/ Fiscal years ended June 30, 1900 to 1917, inclusive. Calendar years 1918-40, inclusive.

3/ 1900-25, inclusive, included in "Other."

4/ Data unavailable, 1900-18, inclusive, and 1926-40, inclusive.

Imports of specified mineral pigments, by principal countries of origin, during 1939 follow.

(Source: Bureau of Foreign and Domestic Commerce)

Item	From main source			Total, From all sources	
	Source	Pounds	Value	Pounds	Value
Red oxide of iron, natural..........	Spain	8,499,737	$ 129,621	10,873,572	$ 171,649
Synthetic iron					305,485
oxide.............	United Kingdom	1/3,010,964	163,564	6,035,150	305,485
Sienna...............	Italy	2,660,649	67,793	2,772,989	74,100
Ocher................	France	6,697,434	78,966	6,930,815	83,560
Crude barite.......	Cuba	23,072,000	55,817	23,175,000	55,985
Vandyke brown....	Germany	905,859	30,555	905,859	30,555
Umber...............	Cyprus	9,006,939	48,550	9,453,493	57,555
Whiting.............	Belgium	14,919,958	38,992	18,755,648	55,025

1/ Probably includes a considerable quantity of processed natural pigments.

UNITED STATES EXPORTS OF MINERAL PIGMENTS

Canada is the best market for pigments containing iron oxide shipped from the United States and buys about 50 percent of the exports of these commodities. The United Kingdom takes about 25 percent. Japan and Italy formerly received small amounts. Canada also imports about half of all other mineral pigments shipped from the United States. The following table shows the growth in export trade in mineral pigments. The noniron-oxide pigments are largely responsible for the growing trade, as shipments of the pigments containing iron oxide have been declining in recent years.

Exports of domestic mineral pigments from the United States[1/]

Year	Ocher, umber, sienna, and other iron oxide pigments		Other mineral pigments including barite, whiting, etc.		Total	
	Pounds	Value	Pounds	Value	Pounds	Value
1922	27,678,305	$ 972,735	(2/)		27,678,305	972,735
1923	28,584,484	999,177			28,584,484	999,177
1924	28,206,731	823,563			28,206,731	823,563
1925	31,264,521	902,833			31,264,521	902,833
1926	31,954,847	1,006,181			31,954,847	1,006,181
1927	37,292,451	1,125,030			37,292,451	1,125,030
1928	38,733,021	1,083,820			38,733,021	1,083,820
1929	41,132,189	862,570			41,132,189	862,570
1930	45,132,189	535,193			45,132,189	535,193
1931	16,612,378	272,373	16,444,055	$156,982	33,156,433	429,355
1932	6,354,300	177,450	9,083,263	108,636	15,437,563	286,086
1933	6,718,056	142,117	14,889,614	209,859	21,607,670	351,976
1934	21,400,764	273,072	9,147,657	131,951	30,548,421	405,023
1935	27,952,611	278,392	20,378,236	195,491	48,330,847	473,883
1936	29,258,754	333,644	26,624,154	235,187	55,882,908	568,831
1937	13,478,092	375,572	25,170,051	255,080	38,648,143	630,652
1938	11,395,849	302,729	31,776,057	286,960	43,171,906	589,891
1939	10,910,436	299,289	41,048,145	516,337	51,958,581	815,626
1940	10,395,731	347,110	56,331,889	715,100	66,727,620	1,062,210

1/ Data derived from Foreign Commerce and Navigation of the United States, U. S. Bureau of Foreign and Domestic Commerce. Statistics previous to 1922 not available.

2/ "Other mineral pigments" are included in "Ocher, umber, etc." for 1922-30, inclusive.

Exports of ocher, umber, sienna, and other forms of iron oxide for paints (dry) from the United States in 1939

(Source: Bureau of Foreign and Domestic Commerce)

Country of destination	Pounds	Value
United Kingdom........	4,655,555	$ 77,596
Canada	4,057,238	104,519
Argentina	632,628	36,377
Netherlands	202,943	5,554
France	201,976	6,163
Netherlands Indies....	167,078	3,974
Other countries	993,018	65,106
Total	10,910,436	299,289

COMPOSITION OF PAINTS AND VARNISHES

Ordinary paints contain three essential components - the pigment, the vehicle or medium, and the drier or siccative. The ordinary varnish consists of a gum such as kauri, copal, damar, or a synthetic resin dissolved in linseed oil or other drying oil. If a stain is added, the product is a varnish stain. An enamel may be defined as a pigmented varnish, or a paint plus a varnish. Nitrocellulose lacquers and asphaltum paints do not contain a drying oil, though nitrocellulose lacquers may contain castor oil as a plasticizer.

The most common paint vehicle is linseed oil, raw or boiled. Normally tung oil, also known as chinawood oil is next in importance; followed by soybean oil, perilla oil, oiticica oil, dehydrated castor oil, fish oils (principally menhaden and sardine) safflower-seed oil, sunflower-seed oil, and poppyseed oil. Although there was no shortage of linseed oil or of soybean oil before Pearl Harbor, adequate supplies of tung oil at reasonable prices have been very difficult to obtain since 1937 owing to hostilities in the Orient. Most soybean-oil formulas include a certain amount of perilla oil, and shortage of the latter oil, which comes from Manchuria by way of Japan, has held up the consumption of soybean oil in paints. Oiticica oil from Brazil has become a creditable member of the drying-oil family since its commercial introduction about 1935. Dehydrated castor oil, too, is a newcomer, having made its commercial debut in 1939. The latter two oils are important as tung-oil replacements. Even more recent tung-oil substitutes are unsaturated fatty acids and fish oils which have been fractionally distilled to remove saturated components.

The drier, usually a salt of a heavy metal (manganese linoleate, for example), aids in the oxidation and polymerization of the drying oil to a tough, glossy film. This phenomenon is known as "drying". Umbers owe their rapid drying properties to their manganese content.

The interest of the mining industries in paints, enamels, and lacquers is necessarily centered on pigments and extenders. Pigments may be defined as insoluble, opaque powders that may yield paints when admixed with suitable mediums, thereby distinguishing them from dyes and stains, which are soluble in the vehicles. In addition to their use in the paint industry, pigments are consumed in the manufacture of rubber goods, linoleum, oilcloth, artificial leather, paper, printing inks, textiles, cement building materials and plastics. The paint trade, however, affords the main market for pigments.

A good pigment must have hiding power and tinting strength, brightness and clearness of tone, and permanence. It must be unaffected by other pigments or by the vehicle. It must have good body, fineness, ease of manipulation, and be compatible with the vehicle in which it is ground.

Raw: Yellow, yellow-brown Burnt: Red, red-brown, salmon		Dark brown to black
OCHERS	SIENNAS	UMBERS
Fe_2O_3 10 to 30 percent	Fe_2O_3 25 to 75 percent	Fe_2O_3 25 to 47 percent
	MnO_2, small percentage	MnO_2 11 to 23 percent
SiO_2 35 to 50 percent	SiO_2 10 to 35 percent	SiO_2 16 to 35 percent
Al_2O_3 10 to 40 percent	Al_2O_3 10 to 20 percent	Al_2O_3 3 to 13 percent
Loss on ignition, 10 to 12 percent	Loss on ignition, 15 to 20 percent	Loss on ignition, 10 to 15 percent

Figure 1.- Approximate composition of raw-earth pigments.

LEADING KINDS OF PIGMENTS

Pigments may be classified roughly as either (1) chemical or (2) mineral. The principal chemical pigments are compounds of lead, zinc, barium, titanium, and iron. Lead pigments are white lead (basic lead carbonate), sublimed white lead (basic lead sulfate), red lead (lead tetroxide), and litharge (lead monoxide). Zinc pigments are zinc oxide and zinc sulfide, both white. Blanc fixe (precipitated barium sulfate) is the chemical equivalent of the mineral barite. The smaller particle size of blanc fixe makes it a much better pigment than barite. Titanium oxide is a white pigment of great covering power obtained from the mineral ilmenite. There are important mixed pigments, such as leaded zinc oxide, lithopone (a precipitated mixture of barium sulfate and zinc sulfide), and titanated lithopone. Red, yellow, brown, and black synthetic iron pigments are prepared from solutions of iron salts by precipitation and calcination. Less important chemical pigments are precipitated chalk (calcium carbonate), prussian blue (ferric ferrocyanide), ultramarine blue (a complex sodium-aluminum-thiosilicate), chromium pigments (including green chromic oxide and yellow lead chromate), cobalt oxide, and black pigments (such as carbon black and lamp black). Lakes are chemical pigments formed by the precipitation of an inorganic base, such as colorless aluminum hydroxide, in certain dye solutions. The dye is adsorbed physically on the colloidal particles of the base or may act chemically with the base. Lake pigments have excellent color and considerable tinting strength.

The chief natural mineral pigments are the iron oxides; such pigments as graphite and terre verte are much less important. Materials such as ground barite, whiting (ground chalk or limestone), ground slate, and asbestine (ground fibrous talc) are used as fillers or extenders rather than for their meager pigmenting properties.

Iron oxide pigments may be divided into two groups, the natural and the synthetic. This paper is concerned chiefly with the natural, and these are discussed below according to color.

1. Yellow iron oxide pigments. - This group contains both ochers and siennas. Ocher is a form of limonite ($2Fe_2O_3.3H_2O$) mixed with clay. Ochers should analyze 17 to 60 percent Fe_2O_3 (French ochers contain 17 to 24 percent Fe_2O_3) and should have a clean, clear mass tone and tint. Raw siennas (first found in Siena, Italy) contain hydrated iron silicate in addition to the limonite and should analyze 40 to 75 percent Fe_2O_3. Burnt sienna, which has part of the water of hydration driven off, is light yellow to deep or reddish-brown. Ochers grade into siennas with increasing iron content, and the main basis of differentiating the two pigments is the opacity of ocher contrasted to the translucence of sienna. Sienna is more of a stain than a pigment. Synthetic

yellows are made by precipitating hydrated ferrous oxide from a ferrous salt solution by means of an alkali, with subsequent oxidation. The pigments analyze about 85 percent Fe_2O_3 and 15 percent water of hydration.

2. Brown iron oxide pigments. - The most important brown pigment, and the mineral pigment most likely to be found by prospectors, is raw metallic brown or mineral brown (limonite and siderite iron ores). The finished product is made by calcining the raw ore. The high-iron-content ores are more desirable, and manufacturers rarely consider raw ores containing less than 65 percent Fe_2O_3. The usual range for the crude ore is 65 to 72 percent Fe_2O_3, which is increased to over 75 percent when the material is calcined. The color range of metallic browns is wide, ranging from light yellow-brown to deep bluish-brown. Umbers are greenish-brown when raw. The Fe_2O_3 content is 45 to 50 percent; MnO_2, 8 to 15 percent. Burnt umbers should analyze 50 to 54 percent Fe_2O_3 and 8 to 16 percent MnO_2. Siennas grade into umbers with increasing manganese content. Like siennas, umbers are somewhat transparent and are used more as stains or glazes than as pigments. Burnt umber is made by calcining the raw material at 350 to 400° F., which drives off part of the water of hydration and other volatile matter. Burnt umbers are brighter in mass tone and in tint than metallic browns. Synthetic browns are made in two ways, by calcining precipitates from iron sulfate solutions, or by blending red, yellow, and black iron oxides.

3. Red iron oxide pigments. - This class is largely hematite, which for pigment purposes should have a Fe_2O_3 content of at least 60 percent. The brightest red iron oxide that has been discovered is a hematite from the Persian Gulf analyzing 70 to 74 percent Fe_2O_3, the remainder being chiefly siliceous material. Normally, the most widely used natural red pigment is a Spanish hematite containing 81 to 87 percent Fe_2O_3, which is less brilliant than the Persian Gulf hematite. A number of domestic hematites are also used, but none of them are believed capable of permanently replacing the Persian Gulf or Spanish oxides. If a domestic hematite containing 80 percent or more Fe_2O_3, with a deep color in oil equal to or better than that of Spanish oxide and with a low calcium carbonate content, could be found, it would probably find extensive use as a pigment in paints and for other purposes. Synthetic red iron oxides range in color from light yellowish-red to deep maroon and contain 97 to 99 percent Fe_2O_3. They are of two general types, those manufactured by calcining iron sulfate and those made by calcining precipitated iron oxides. In the former class would fall the Venetian reds, analyzing about 60 percent CaO and about 40 percent Fe_2O_3, made by calcining iron sulfate and calcium sulfate obtained from pickling liquor solutions (acid residues used to clean sheet iron) neutralized with lime.

4. Black iron oxide pigments. - The natural black iron oxides are magnetites, and the only grades for which commercial use has been found are fairly pure, analyzing 90 to 95 percent Fe_2O_4. Even these have poor color value in comparison with synthetic black oxides that are precipitated from ferrous sulfate solutions and analyze 98 to 99 percent Fe_3O_4.

Terre verte or green earth, is a natural earth consisting principally of the mineral glauconite and owes its color chiefly to the iron silicate present. The pigment is durable but has poor opacity and is quite dull. The principal deposits (near Verona, Italy) are believed to be virtually exhausted.

Pure graphite is unsuitable as a paint pigment, as it tends to coagulate in the oil vehicle and to spread under the brush into an excessively thin coating. Impure graphite containing substantial quantities of silica, on the other hand, can be mixed with iron oxide or zinc compounds to give a satisfactory pigment. In Michigan and elsewhere graphitic rock has been ground directly into pigment, and the product often contains as little as 25 percent graphitic carbon.

Extenders or fillers used in the paint industry consist chiefly of ground limestone, asbestine (fibrous talc), barite, silica, slate flour, shale flour, gypsum, diatomite, magnesite, witherite, mica, and numerous other materials. The value depends on purity and color characteristics. Of particular interest in this group is asbestine, which keeps the body of the paint good and prevents the pigment from settling. The demand for asbestine is excellent, and material of high purity would probably find a ready market.

STANDARD SPECIFICATIONS

There are several sources of pigment specifications, but those most frequently referred to are prepared and distributed by the United States Procurement Division, the United States Navy Department, the United States War Department, and the American Society for Testing Materials. These various specifications are, in general, quite similar.

In Federal Specification TT-O-111, "Ocher; dry, paste-in-Japan, and paste-in-oil", released by the Procurement Division, the ocher is required to be "a hydrated oxide of iron permeating a siliceous base." A minimum Fe_2O_3 content of 17 percent and a 5-percent maximum of calcium compounds (as CaO) are permitted. No lead chromate or organic colors may be added. Particles remaining on a 325-mesh sieve must not exceed 1 percent.

Sienna requirements are outlined in Navy Department Specification 52S4d are similar to those for ocher, except that moisture content is limited to 4 percent, and the plus-325-mesh content permissible is 3 percent.

Specifications for umber (Navy Department Specification 52U1e) describe the pigment as a hydrated oxide of iron and manganese permeating a siliceous base, free from organic coloring matter, containing not more than 5 percent of calcium compounds calculated as CaO, not more than 4 percent moisture, and not more than 3 percent of coarse particles retained on 325-mesh sieve.

Federal Specification TT-P-31, paints; Iron-hydroxide and iron-oxide ready-mixed and semipaste, permits the addition of carbon black to iron oxides but prohibits organic coloring matter, either dyes or lakes. The Fe_2O_3 minimum is 30 percent,[3/] and the total of ferric oxide, insoluble siliceous matter, and loss on ignition should not be less than 90 percent.

All of the specifications mentioned above have additional requirements for mass color, tinting strength, and oil absorption based upon a standard sample obtainable from the respective agencies.

The bulk density of powdered natural pigments usually ranges from 25 to 50 pounds per gallon, and linseed-oil absorption is from 14 percent for finely ground natural colors of high iron content to 70 percent or more for semicolloidal, precipitated colors. For American ochers, the range in oil absorption is from 35 to slightly more than 50 percent. Methods of determining oil absorption may be found in many of the Federal specifications and in such standard reference works as Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors, by Henry A. Gardner.

Several specifications for paints, pigments, and methods of testing them have been prepared by the American Society for Testing Materials, 260 Broad St., Philadelphia, Pa., and may be obtained from the Society at a cost of 25 cents each. Typical specifications and testing procedures are:

A.S.T.M. Designation D-85-27, Standard Specifications for Ocher.

A.S.T.M. Designation D-84-40, Standard Specifications for Mineral Iron Oxide.

3/ In a proposed revision, Federal specification TT-P-31a, the minimum Fe_2O_3 content is 60 percent.

A.S.T.M. Designation D-34-39, Chemical Analysis of White Pigments. (Includes white chemical pigments, whiting, barite, and china clay.)

A.S.T.M. Designation D-50-36, Chemical Analysis of Yellow, Orange, Red, and Brown Pigments Containing Iron and Manganese. (Includes Indian reds, red oxides, ochers, siennas, umbers, and Venetian red.)

A.S.T.M. Designation D-185-37, Standard Method of Testing for Coarse Particles in Pigments, Pastes, and Paints.

A.S.T.M. Designation D-280-33, Standard Method of Test for Hygroscopic Moisture (and Other Volatile Matter under the Test Conditions) in Pigments.

A.S.T.M. Designation D-281-31, Standard Method of Test for Oil Absorption of Pigments.

A.S.T.M. Designation D-153-39, Standard Method of Test for Specific Gravity of Pigments.

A.S.T.M. Designation D-387-36, Standard Method of Test for Mass Color and Tinting Strength of Color Pigments.

Some pertinent Government specifications not mentioned above are:

War Department:

Indian red, Specification 3-35-B.
Venetian red, Specification 3-37-B.
Umber, Specification 3-39-A.
Sienna, Specification 3-40-A.

Navy Department:

Indian red, Specification 52-R-3c.
Venetian red, specification 52-R-4d.

OCCURRENCE

Ochers have been produced in Georgia in the Cartersville district, Bartow County, since 1877, when E. H. Woodward began mining operations. Most of the domestic ocher is produced in Georgia, and it is estimated that present output in the State is about 15,000 tons annually. Virginia has produced ocher intermittently for 75 years or more; extensive deposits exist in several parts of the State. Production is probably 5,000 to 7,000 tons annually. In Pennsylvania, yellow ocher occurs at many places, although it is worked mainly in the eastern part of the State in Northhampton, Lehigh and Berks Counties. Production is estimated at 4,500 tons annually. In Vermont, beds of ocher in Rutland and Bennington Counties have been worked from time to time in the past. In Alabama, ocher is mined in Clark County. In California, ocher deposits have been worked in Calaveras, Napa, and Riverside Counties.

Deposits of umber have been worked near Bethlehem, Doylestown, and Bethel in Pennsylvania, and sienna has been produced near Reading, Pa., and at Valley Station near West End, N. J. Umber could be produced also in the ocher and manganese district in the vicinity of Cartersville, Ga., if the demand existed. A good deal of umber is associated with barite deposits in Virginia and some was shipped experimentally in 1940.

Of the iron oxides, only hematite (Fe_2O_3), and limonite ($2Fe_2O_3.3H_2O$) are employed extensively as pigments. Hematite occurs as Clinton hematite or red hematite in Tennessee and Alabama and represents the larger part of the red iron oxide pigments produced in the United States. Limonite deposits are numerous throughout the United States. Fairly pure limonite derived from iron-bearing limestones often has commercial value, and such deposits are found along the Appalachian Mountains from western Massachusetts southward into Alabama. Limonite deposits of various kinds are found throughout the Western States, but as yet they have not been developed extensively.

Approximately 350,000 short tons of crude barite is produced annually in the United States, and about half of this quantity is converted into ground barite. Only a small percentage of the latter is used as a pigment, however. Domestic deposits were worked in Missouri before the World War of 1914-18, but consumers along the Atlantic seaboard depended upon imports from Germany because of cheaper freight. World War I paved the way for successful barite mining in Georgia in the Cartersville area.

Both amorphous graphite and crystalline flake graphite have been mined in many States, but graphitic slates near L'Anse, Mich., and a deposit south of Carson City, Nev. supply most of the graphite used in paint.

METHODS OF TREATMENT

The crude pigment as it comes from the mine must be refined before it can be used in a paint. The soft, claylike pigments may be washed or given other simple treatments. The harder materials, including shales, may be ground in hammer mills, which may or may not be equipped with accessory devices for throwing out hard impurities. Pulverizers such as ball mills also are used. Roller mills may be used for the softer materials. Buhr mills formerly predominated the field but today are being abandoned. Wet-ground materials are sized by levigation and dry-ground pigments by air separation. A southern ocher mill spatters the overflow from the slurry on revolving drums heated with steam under 80 pounds of pressure. The ocher is scraped off mechanically as soon as it is dry. In this way the material is dried uniformly, and no portion of it is darkened. Vertical shaft kilns, rotary furnaces, platform calciners, or floor kilns may be used in making burnt ochers, metallic paints, and the like. Sometimes, to render the tone more vivid, artificial pigments or aniline dyes are added.

DOMESTIC PRODUCTION OF MINERAL PIGMENTS

It is difficult to establish an accurate trend in the production of mineral pigments. Statistics were compiled and published by the Geological Survey from 1880 to 1915, showing annual production of domestic mineral pigments, but were incomplete during the first few years of the canvasses. Data published by the Bureau of the Census, though up-to-date have in the past covered different commodities in different commodities in different years, preventing accurate comparisons in the same commodities from year to year. The iron oxides seem to be produced at a fairly constant rate of nearly 100,000,000 pounds annually, while more variation in production is found in the other mineral pigments.

The accompanying tables indicate the production of mineral pigments in the United States during the past 40 years.

Production of mineral pigments
(From Mineral Resources of the United States, Geological Survey, U. S. Department of the Interior)

	Ocher		Umber and sienna		Metallic paint		Mortar color		Venetian red		Slate, including mineral black		Total	
	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value	Short tons	Value
1900	17,015	$186,707	2,409	$41,698	23,218	$261,831	6,689	$ 79,911	14,696	$236,574	6,395	$ 53,942	70,422	$860,663
1901	16,711	177,799	1,064	20,630	15,915	204,937	9,346	112,943	9,201	153,467	4,865	41,211	57,102	710,987
1902	16,565	145,708	669	15,546	19,020	313,390	8,355	98,729	11,758	196,905	4,071	39,401	60,438	809,679
1903	12,524	111,625	666	15,367	25,103	213,109	10,863	101,792	7,425	134,635	7,106	59,029	63,687	635,557
1904	16,826	110,602	522	12,960	19,357	204,377	7,525	84,426	7,449	137,737	5,370	53,709	57,049	603,811
1905	13,402	126,351	689	17,004	16,489	176,722	10,494	120,430	6,879	137,541	5,181	44,108	53,134	622,156
1906	15,482	148,049	657	17,394	17,992	204,026	10,309	111,720	13,526	198,394	5,481	40,540	60,509	703,508
1907	14,354	153,417	545	11,304	15,048	181,693	9,490	97,719	7,566	134,167	12,702	92,130	59,620	671,481
1908	14,696	140,439	1,212	30,705	14,022	156,694	7,856	72,881	8,825	159,650	12,617	93,181	59,228	653,550
1909	12,458	125,349	1,276	33,472	20,722	201,905	10,820	108,126	8,358	145,733	14,944	98,176	68,578	712,761
1910	11,711	112,445	1,015	26,700	29,422	184,869	9,960	107,780	6,312	113,980	16,515	96,001	75,041	643,478
1911	11,703	109,465	1,005	26,225	25,599	181,163	7,922	76,517	5,773	106,009	16,510	105,451	68,512	604,830
1912	15,269	149,289	805	21,975	28,347	181,352	9,272	87,595	6,306	116,511	20,964	121,482	80,962	678,204
1913	17,578	173,944	776	20,790	30,098	171,264	5,357	35,443	6,171	116,195	16,786	110,969	76,766	628,605
1914	14,387	136,185	790	21,070	30,947	179,653	5,371	47,723	7,445	119,895	15,271	88,405	74,211	592,931
1915	(1/)	(1/)	(1/)	(1/)	(1/)	(1/)	(1/)	(1/)	(1/)	(1/)	(1/)	(1/)	2/57,442	2/551,598

1/ Not available.
2/ Partly estimated. Includes ocher, sienna, metallic paint, mortar colors, and ground slate and shale.

Domestic production of mineral pigments[1/]

Year	Pigments containing iron oxide				Other	
	Natural (ochers, siennas, metallic brown, etc.)		Synthetic			
	Pounds	Value	Pounds	Value	Pounds	Value
1899	2/ 34,904,000	$367,987	(6/)		(6/)	
1904	48,826,000	336,616	(6/)		(6/)	
1909	213,285,734	1,085,438	(6/)		(6/)	
1914	92,896,956	797,819	(6/)		(6/)	
1919	202,181,787	3,778,942	(7/)		38,263,989	$1,176,505
1921	82,757,631	1,737,478	2,370,757	$214,409	51,837,136	709,939
1923	122,000,759	2,718,088	4,907,251	415,865	144,890,761	2,349,082
1925	78,045,165	1,517,997	10,726,367	866,151	41,107,234	858,307
1927	96,676,202	2,452,134	11,681,533	905,761	29,199,617	343,884
1929	3/105,627,130	3,374,800	(7/)		4/ 17,263,000	254,373
1931	64,212,191	1,943,110	(7/)		2,811,213	41,308
1933	61,954,000	2,069,000	(6/)		(6/)	
1935	112,423,238	3,079,206	(8/)		5/275,200,997	20,255,865
1937	128,891,324	4,067,840	(8/)		152,105,207	6,688,338
1939	101,949,630	3,275,941	(8/)		31,207,511	1,644,802

1/ Data taken from Census of Manufactures, Bureau of the Census.
2/ 1899 to 1914, inclusive, is production of iron buff and other earth colors.
3/ 1929 to 1933, inclusive, is production of all forms of natural iron oxide pigments except mortar colors.
4/ Includes zinc sulfide and mortar colors.
5/ 1935 and 1937 excludes production of whiting.
6/ No data available.
7/ Included in "Other."
8/ Included in "Natural."

OPPORTUNITIES FOR DOMESTIC PIGMENTS

In appraising a mineral-pigment deposit for possible development, certain essentials should be borned in mind. The buyer judges red hematites and yellow ochers principally upon the basis of original color, which is unchanged in processing. On the other hand, original color is not as important in metallic brown, a limonite pigment, but the material must have a ferric oxide content of 65 percent, and a claylike texture is preferred to hard or gritty ore or gangue; the color can be adjusted in roasting. Siennas should have a high degree of transparence. In the dark-brown to black pigments the ferrosic oxide content, Fe_3O_4, is the most important consideration; this should not fall below 90 percent.

The size of the deposit, nearness to consuming centers, and cost of mining must also be considered.

The more progressive pigment manufacturers examine carefully by means of calcination tests and quantitative iron analysis all domestic iron oxide pigments sent them. From the hundreds of specimens submitted annually, from time to time a material is found which makes a satisfactory pigment at a profit to both producer and processor.

MINERAL PIGMENTS IN FOREIGN COUNTRIES

Mineral-earth pigments of long-established reputation are produced in France, Spain, Cyprus, Italy, and on the Island of Hormuz in the Persian Gulf.

The principal ocher deposits of France are situated at two main centers - Apt, in the Department of Vaucluse, and Auxerre, in the Department of Yonne.

A full color range of pigments is produced, from light canary yellow to the deepest reds. The yellow ochers are obtained in the Vaucluse field by both farmers and mill owners. Farmers who have enough water usually wash the ore before hauling it to the Apt market. The ore is dug during the fall, stored, washed in dammed-up streams during the rainy season (January to April), and dried in covered sheds from April to July. Factory refined ocher undergoes treatment by methods basically similar to those used by farmers. The material is washed in large concrete basins and ground, cleaned, bolted, sorted, and graded mechanically.

During the nineteen-twenties French shipments of ochers to the United States averaged 16,000,000 pounds a year. In the thirties, however, shipments dropped to about 7,000,000 pounds annually. The decrease was caused by competition with the new American synthetic ochers and fortified natural ochers. Some pigment producers believe that French ochers will be even less important after the cessation of hostilities in World War II. French ochers are rather coarse, are hard to grind, and have very low coloring value in comparison with the improved standards developed by the American paint industry during the past few years. The successor to the French ocher is a domestic natural yellow ocher fortified with precipitated iron yellow. The product has a strong coloring power, is uniform, and is easy to grind.

Italian sienna likewise enjoys a worldwide reputation; the output comes principally from Tuscany. The Harz Mountains in Germany are the only other important source of supply, although small quantities are produced elsewhere, notably in Sicily. The Sicilian product, however, is shipped to the mainland of Italy for further treatment. The chief producing centers in recent years are in the Provinces of Verona, Cagliari, and Grosetto. Leghorn for many years has been the marketing center for Italian siennas, and much of the crude earth is prepared there.

Turkish umber is produced chiefly in the Lanarka district of the Island of Cyprus. Virtually the entire output of Cyprus is exported. In normal times exports average 5,000 to 6,000 tons annually; the United States purchases about half.

Spain is one of the most important producers of natural red oxide of iron for use in paints. The principal deposits are in eastern Andalusia in the interior Province of Jaen, where it is produced partly as a byproduct in mining iron ore, with which it occurs. The iron oxide occurring in this Province is a variety of red hematite containing 81 to 87 percent of ferric oxide and is the standard grade of "Spanish red oxide," with extreme brilliance and covering power. There are two or three plants in the interior but most of the crude pigment is shipped to Malaga for grinding. From Malaga the pigment is shipped to world markets.

A red oxide of iron of rich color and high quality is produced on the Island of Hormuz in the Persian Gulf under a Persian Government monopoly. Domestic substitutes for this oxide are neither so good nor so cheap as the Persian product and doubtless will give way to it when the war is over.

The famous chalk beds of northwestern Europe, including Britain, France, and Belgium, supply most of the world's requirements of whiting. In England the industry is centered in Kent. The quarried chalk is placed in a washing tank and pulverized by means of iron bars suspended from rotating arms. The material is screened, and only that which passes 180-mesh wire gauze is used. The fine slurry is conveyed to settling pits, dried, and bolted.

Half of the world supply of barite is produced in Germany, and normally more than half of the German output is exported, large quantities of crude barite being shipped to the United States, Great Britain, France, Netherlands, and Belgium. The German barite industry is centered in Prussia; much smaller quantities are produced in Bavaria. Great Britain, Italy, and Australia also produce considerable quantities of crude barite. During the last few years deposits in Cuba have been opened and constitute the leading source of imports of barite to the United States.

PRICES

The producer of mineral pigments may sell the crude material to a refiner or the larger producer may prepare the pigment for market himself. The prices for some typical, refined mineral pigments are shown below, indicating trends since 1919. The products quoted are of American origin.

Prices of refined, domestic, natural pigments[1/]

Pigment	Prices, in cents per pound				
	Jan. 1, 1919	Jan. 7, 1929	Jan. 1, 1934	Jan. 2, 1939	Sept. 15, 1941
Yellow ocher ....bbl., works, lb.	(2/)	1-5/8 to 2-5/8	1-3/8 to 2-5/8	1-1/2 to 2-3/4	2 to 2-1/4
Metallic brown..................do.........	1-1/5 to 1-3/5	1-4/5 to 2-1/5	1-4/5 to 2-1/5	2-1/4	2-1/2 to 3
Burnt sienna....................do.........	3-1/2 to 4	2-7/8 to 3-1/2	2-7/8 to 3-1/2	3	3-1/2 to 5
Umber..........................do.........	3-1/2 to 4	2-7/8 to 3-1/2	2-7/8 to 3-1/2	2-7/8	3-3/4 to 4-3/4
Red iron oxide ....do.........	1-1/4 to 3	1-1/2 to 3-1/2		1-1/2 to 3-1/2	1-1/2 to 4

1/ From Oil, Paint, and Drug Reporter and other sources.
2/ Item not listed in price schedules.

POSSIBLE BUYERS OF CRUDE MINERAL PIGMENTS

California (Emeryville):

C. K. Williams Co.

Georgia (Cartersville):

New Riverside Ocher Co.
Frank Smith

Illinois (Chicago):

Tamms Silica Co., 228 N. LaSalle St.

Maryland(Muirkirk):

Mineral Pigments Corporation, Washington Blvd.

Michigan (Detroit):

Baker & Collinson, 6545 Georgia Ave.

New York (New York City):

Georgia Peruvian Ocher Co., 165 Broadway.
Hammill and Gillespie, 225 Broadway.
National Lead Co., 111 Broadway.
Reichard-Coulston, Inc., 95 Madison Ave.
J. Lee Smith & Co., Inc., 23 Jacob St.

Pennsylvania:

Prince Manufacturing Co., Bowmanstown.
C. K. Williams, 640 N. 13th St., Easton.

Tennessee (Chattanooga):

Lookout Paint Manufacturing Co., Alton Park.

Virginia (Henry):

Blue Ridge Talc Co., P. O. Box 7.