

DETERMINATION OF THE SULFUR OF VULCANIZATION—If the statement of Alexander¹ proves to be true, that the sulfur of vulcanization of the rubber remains quantitatively in the nitrosite, this method could possibly admit of the simultaneous determination of the sulfur of vulcanization. An aliquot portion of the clear acetone solution of the nitrosite would be evaporated to dryness, and the sulfur determined in the usual way.

RESULTS—The following results were obtained by the method above described. All are given that have been obtained on good quality, soft-vulcanized compounds since the date after which no great changes in the procedure were made. Whether the method is applicable to compounds of poor quality has not been determined, and as the author is no longer in a position to work on this point the field must be left to others. This Bureau may be able, however, to work in this field at some later date.

- A. A washed and dried Up-river Fine gave 94.0, 95.1, 95.8 and 95.9 per cent $C_{10}H_{16}$.
Average = 95.2 per cent plus 3.3 per cent acetone extract = 98.5 per cent.
- B. A commercial compound containing 45 per cent Fine Para gave 42.0, 42.2, 42.7, 43.1, 43.3 and 43.4 per cent $C_{10}H_{16}$.
Average = 42.8 per cent plus 1.3 per cent acetone extract = 44.1 per cent.
- C. A commercial compound containing 48 per cent Fine Para gave 44.8, 45.1, 45.1 and 45.3 per cent $C_{10}H_{16}$.
Average = 45.1 per cent plus 2.4 per cent acetone extract = 47.5 per cent.
- D. The same compound after standing finely ground for a month gave 43.4, 43.5, 43.5 and 45.0 per cent $C_{10}H_{16}$.
Average = 43.7 per cent.
- E. A commercial compound containing 25 per cent Fine Para and 20 per cent Caucho or 45 per cent gum gave 40.3, 40.4, 40.6 and 41.1 per cent $C_{10}H_{16}$.
Average = 40.6 per cent plus 3.2 per cent acetone extract = 43.8 per cent.
- F. A commercial compound containing 41.5 per cent Coarse Para gave 39.5, 39.6, 39.8 and 40.1 per cent $C_{10}H_{16}$.
Average = 39.8 per cent plus 2.1 per cent acetone extract = 41.9 per cent.

SUMMARY

A new method for the direct, determination of rubber is described, which is based upon the combustion of the nitrosite of rubber in a current of oxygen, and weighing of the carbon dioxide thus formed. The results indicate a fair degree of reliability for both raw rubber and high-grade vulcanized compounds. The use of this method for the analysis of low-grade compounds and for the simultaneous determination of sulfur of vulcanization may be possible if its application to these fields is further studied.

During this work many valuable suggestions were made by Dr. W. F. Hillebrand, Mr. J. B. Tuttle, and a number of others at this Bureau, and I take this opportunity to express to them my appreciation of the same.

BUREAU OF STANDARDS
WASHINGTON

OSAGE ORANGE—ITS VALUE AS A COMMERCIAL DYESTUFF²

By F. W. KRESSMANN

INTRODUCTION

This study is the result of an investigation on the utilization of osage orange mill waste.

The trunk of the osage orange tree is rather small in size, misshapen, and generally defective as a saw

¹ *Z. angew. Chem.*, **20** (1907), 1364; **24** (1911), 687; *Ber.*, **40** (1907), 1077.

² Presented at the 49th meeting of the A. C. S., Cincinnati, April 6-10, 1914.

log; and, although because of the valuable properties of the wood (for wagon felloes especially) closer utilization will scarcely be found in the use of any other wood, comparatively large amounts of waste are produced annually.

Osage orange has long been used in Texas in a small way as a dyewood. The roots, bark, and wood are chipped and boiled with water and a more or less permanent yellow is obtained from the extract. Sargent¹ mentions the root bark as a source of a yellow dye and it has even been suggested by some² that osage orange is superior to fustic in its dyeing qualities, although no actual comparative experiments between fustic and osage orange seem to have been recorded.

In view of these facts, it seemed advisable not only to determine the chemical nature of the dyestuff but also its dyeing value as compared with the commercial dyewood it resembles most, namely, fustic.

A qualitative study of the aqueous extract obtained from the wood showed that the dyeing principles present were, as in fustic, morin or moric acid, and morintannic acid or maclurin. From a preliminary series of dyeing experiments made at this laboratory, it was found that osage orange, like fustic, is a poly-genetic mordant dyestuff.

Since the wood seemed to contain a sufficient amount of dye to give it commercial value, a series of comparative dyeing experiments on fustic and osage orange were arranged so as to determine as accurately as possible the value of osage orange in terms of a well-known standard such as fustic. In order to have these experiments performed at institutions best equipped for the purposes and also to obtain the results of a number of different workers in this field, the coöperation of a number of the leading textile schools³ of the country was sought and the writer wishes to take this opportunity to thank them for their coöperation and assistance.

COMPARISON OF DEPTH OF COLORS PRODUCED

REPORT A—"It was noticed that dyeings produced with osage orange were weaker than those obtained with fustic under the same conditions. Since the osage orange produced a shade of color slightly different from the fustic in most cases, it is difficult to determine the exact relative strength of the two products. It seems, however, that the osage orange contains something like 20-25 per cent less coloring matter than the fustic."

REPORT B—"Dyeings were made under identical conditions on chrome mordanted worsted yarn with the same amounts of both the wood and solid extracts of both substances (*i. e.*, fustic and osage orange).

"The osage orange wood gave the heaviest shades

¹ Sargent, Chas. S., "Manual of the Trees of North America."

² U. S. Dept. of Agr., *For. Serv. Cir.* **184**, "Fustic Wood, Its Substitutes and Adulterants," by G. B. Sudworth and C. D. Mell.

³ Philadelphia Textile School. New Bedford Textile School. Lowell Textile School. The North Carolina College of Agriculture and Mechanical Arts. Georgia School of Technology. Osage orange sawdust furnished by Mr. L. C. Bumpus, Farmersville, Texas.

⁴ Reports on the experiments, giving the results of their test, were submitted by the coöperators, and the information given in this article is in the form of extracts taken from these reports. The reports are designated by letters, this designation being used to separate the extracts.

but, like fustic wood, the yellow obtained had a reddish cast.

"With the extracts, the yellow obtained in each case was of a greenish tone; but that of the osage orange extract, while not so heavy as that given by the fustic extract, was of a much purer tone, the fustic being rather muddy."

REPORT A—"The dyeing properties of Old Fustic and osage orange are very similar, as will be seen by comparing the shades given on various mordants by the two dye-woods."

COMPARISON OF AMOUNT OF EXTRACT

REPORT C—"Upon extraction with water, osage orange sawdust was found to give a water-soluble extract in the proportion of 7.5 grams of extract for every 100 grams of sawdust."

REPORT B—"A sample each of the osage orange and of chip fustic was dried to constant weight and the moisture was found to be:

	Per cent
Osage orange sawdust.....	9.70
Fustic.....	7.92

"The dried samples were then extracted with methyl alcohol and gave the following amounts of matter extractable with methyl alcohol:

	Per cent of the dry sample
Osage orange sawdust.....	26.63
Fustic.....	12.71

"The residue in each case was then extracted with

shade of yellow, with chromium mordant a tan color, and with iron mordant a dark brown."

REPORT E—"The following table shows the results obtained by dyeing osage orange and fustic wood under the same conditions on wool mordanted with the indicated metallic salts:

PREPARATION OF WOOL SAMPLE	TABLE I		REMARKS
	DYED WITH FUSTIC	DYED WITH OSAGE ORANGE	
Unmordanted	Light yellow	Light yellow	Color produced of no value
Tin mordant	Light yellow	Light yellow	Color more pronounced than above. More reddish with fustic
Alum mordant	Bright yellow	Bright yellow	Yellower and brighter with the osage orange
Iron mordant	Dark olive	Dark olive	Not so deep and slightly greener with the osage orange
Chrome mordant	Orange-yellow to old gold	Orange-yellow to old gold	Fustic sample more reddish and deeper in tone than orange

FASTNESS TO LIGHT, WEATHER, WASHING, ETC.

REPORT E—"The colors produced by dyeing on alum and tin mordanted material were fairly good in appearance but were inferior in fastness to light, especially as compared with colors obtained with the first two salts (iron and chromium). Table II shows the result of test made on dyed samples of osage orange and fustic wood with respect to fastness to light and weather.

"It was noticed that the chrome mordanted samples showed a fastness in this respect superior to that of the other samples. The length of exposure necessary

TABLE II

	FUSTIC WOOD Time exposed			OSAGE ORANGE WOOD Time exposed		
	5 days	10 days	15 days	5 days	10 days	15 days
Direct dyeing	Faded	Color gone	Faded	Color gone
Alum mordant	Slight fading	Faded	Slight fading	Faded
Tin mordant	Slight fading	Faded	Slight fading	Faded
Chrome mordant	No change	Very little if any change	Slight	No change	Very little if any change	Slight

water. The osage orange gave so little matter extractable by water that the amount was not determined. Fustic, on the other hand, gave 4.71 per cent of the dry weight. Therefore, the total extractable matter was:

	Per cent
Osage orange sawdust.....	26.63
Fustic, 12.71 \times 4.71.....	17.42

REPORT E—"The results obtained from experiments made clearly show that the osage orange product does contain a dyeing principle which is very similar in most respects to that found in fustic wood, and also this principle is found in a quantity sufficient to give the orange wood some commercial value as a dye-stuff."

CHARACTER OF DYEINGS

REPORT D—"It would appear that this substance (osage orange) could be advantageously used for self shades also in conjunction with logwood, other mordant dyes (*i. e.*, other natural mordant dyes), as well as with alizarine. Its dyeings are mono-chroic. If made in the form of a water extract it could be used for printing for yellows, browns, greens, and chocolates."

REPORT C—"It was found that this coloring matter was of a polygenetic character, giving, with a tin mordant, a comparatively bright shade of yellow, with aluminum mordant a somewhat duller and greener

to completely destroy the color in each case on the chrome mordant was not determined, it being simply noted that samples from each product showed very nearly the same resistance to fading for time exposed. During this time the fustic was possibly more affected than the osage orange in that there was a tendency for the color to lose some of its reddish cast.

"Samples dyed with fustic and osage orange were examined as to their fastness to washing tests, the samples in each case showing a fairly good fastness in this respect."

REPORT D—"This substance (osage orange) was found to dye level shades of good purity and brightness on wool mordanted with chromium in the usual manner. These dyeings show good fastness to light, water, and washing."

REPORT C—"These dyeings (with osage orange) were exposed to the light for a period of six weeks, and to combined light and weather for a period of 8 weeks. With both chromium and iron mordants the dyeings show very little change at the end of 5 weeks' exposure to sunlight. With aluminum and tin mordants the dyeings show the effect of sunlight in from one to two weeks, becoming much duller. The exposure of the sample dyed with the iron mordant to light and weather for 8 weeks shows very little change. That with chromium mordant for 8 weeks

loses its brilliancy to a considerable extent, although it does not become much lighter in color. The dyeings by aluminum and tin mordants are decidedly changed by this exposure to light and weather. The dyeings by chromium and iron mordants are sufficiently fast to prove of practical value, assuming that the coloring matter could be prepared cheap enough."

SUMMARY AND CONCLUSIONS

I—The quantity and quality of the dyestuff present in osage orange is almost identical with that of fustic.

II—Osage orange may be employed as a dyewood in all cases where fustic wood is used at present. The yellows produced by direct dyeing or by aluminum and tin mordants are too fugitive to be of commercial value. But the orange-yellows, old gold, deep tan, olive and chocolate shades obtained with chromium and iron mordants are equal to, if not better than, those obtained with fustic and are of sufficient fastness to be of commercial value.

III—A domestic source of a yellow dyewood has been found that can advantageously replace a foreign material used at present. The mill waste alone from the present manufacture of osage orange amounts to over 25,000 tons annually; and if this waste could be set down in the East for \$10 to \$12 per ton it is believed that it could compete successfully with fustic, both from cost of production and quality of color produced on dyeing.

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THE RESERVE SUPPLY OF PHOSPHATE ROCK IN THE UNITED STATES

By W. H. WAGGAMAN¹

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Numerous estimates have been made from time to time on the tonnage of phosphate rock available for future use in this country. These estimates vary so widely that little importance has been attached to them, and in many cases they can hardly be considered as anything more than wild guesses.

Owing to the pockety nature of many of our deposits of phosphorites or amorphous phosphates, careful surveys and thorough and systematic prospecting are necessary to gain anything like an accurate knowledge of their value and extent. The expenses of such examinations are frequently not warranted and are seldom made except immediately before actual mining operations are begun. Again, much of the phosphate property has been acquired so cheaply that only a superficial examination was necessary to justify its purchase. Under such circumstances the owners of the land may have but a hazy idea of the amount of phosphate contained therein. On the other hand, some of the phosphate deposits, such as those in our western states and in certain parts of Arkansas and Tennessee, are of such a character that fair approximations of their tonnage might be made by careful surveys.

¹ Scientist in Investigations of Fertilizer Resources.

For some time it has been obviously desirable that both producer and consumer should have some idea (even though a rough one) of the amount of phosphate rock still unmined in the United States. Again and again disquieting reports have been spread that our supplies of this mineral, so important to the American farmer, were being rapidly depleted, and that thereby the agricultural interests of this country would soon be seriously impaired. Alarm has also been caused by the fact that several phosphate companies are owned by European capitalists, and fears have been expressed that foreign capital is seeking to acquire control of the American deposits. It has been urged even that some legislation be enacted preventing the exportation of phosphate rock.

In order to show the actual basis for such reports and whether or not there is any real need for curtailing foreign shipments of phosphates, the data herein contained were collected and compiled with considerable care. The figures were obtained by correspondence and consultation with mine owners and operators, and by direct observation and field investigations of the various deposits throughout the country. So little development work has been done in Kentucky and Arkansas that the tonnages given for these states are thought not to be close; they are regarded, however, as ultra-conservative.

The estimates given below are for rock grading from 58 to 78 per cent "bone phosphate of lime." In the case of the low-grade phosphate in the West and the wash heaps of Florida, the material is figured to its equivalent in high-grade rock.

	Tons
Utah, Idaho, Wyoming and Montana:	
High-grade.....	2,500,000,000
High-grade equivalent of all grades.....	7,500,000,000
Florida:	
High-grade equivalent of all grades.....	354,300,000
High-grade equivalent of wash heaps.....	20,000,000
Tennessee:	
High-grade equivalent of all grades.....	115,075,000
South Carolina:	
High-grade equivalent of all grades.....	10,000,000
Arkansas:	
High-grade equivalent of all grades.....	20,000,000
Kentucky:	
High-grade equivalent of all grades.....	500,000
Total.....	10,519,875,000

The production of phosphate in 1912, according to the figures of the United States Geological Survey, was as follows:

	Tons
Florida.....	2,406,899
Tennessee.....	423,331(a)
South Carolina.....	131,490
Western states.....	11,612(b)
Total.....	2,973,332

(a) Includes production of Arkansas.

(b) Includes Utah, Idaho and Wyoming.

Even assuming that there are to be no new discoveries in this country and that the average consumption during the life of the phosphate fields will be three times its present consumption, there is sufficient to last for over 1100 years provided proper mining methods are employed and means for utilizing the lower grade material are devised.

Another feature of the phosphate industry which in recent years has become of considerable interest to the operator, the fertilizer manufacturer, and the farmer, is the growing use of raw ground rock phosphate for direct application to the field. While the