In our own works, therefore, we have felt it better to use, instead, the total hours worked per accident; and if we say that in a certain department there has been one accident per month for every 21,600 hours worked, or, since the full-time man averages 206 working hours per month, that one man out of approximately every one hundred gets hurt each month, it is something they can grasp. Similarly, we use the average actual hours lost per accident as a measure of accident severity, and it is quite evident the workers will the more readily understand when we say the fellows hurt last year were "knocked out" for 72 hours each or an average of a week and a half, than they will if we tell them their severity rate is 0.27 as compared with 0.29 last year.

How Fatal Accidents and Permanent Disability are Reckoned

If in your plant you had among the accidents one fatality, how would you take it into account in estimating the severity? Or, if an accident resulted in permanent total or permanent partial disability, how would it be included? A careful study of these matters by the International Association of Industrial Accident Boards and Commissions has led them to establish a scale of time losses or disability ratings varying with the degree of disability, death, or permanent disability, representing a time loss of 6000 days. Accordingly, if in figuring your accident severity rate for any given period you had twenty nonfatal accidents with a total loss in time of 100 days and, in addition, one fatal accident, you would have to consider your accidents as 21 with a total loss of 6100 days. Similarly, if an accident resulted in permanent total disability, the amount of the loss would be the same. Still further, if an accident produced permanent partial disability, as the dismemberment of an arm above the elbow, or the permanent disability of any one finger, the losses would be 4500 or 300 days, respectively.

Effect of Yellow and Brown Iron Oxide Pigments upon Rate of Oxidation of Linseed Oil[1]

By F. H. Rhodes and J. D. Cooper, Jr.

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THE effect of certain of the red iron oxide pigments upon the rate of oxidation of linseed oil has been studied by Rhodes, Burr, and Webster.[2] The investigation described in the present article was undertaken for the purpose of obtaining corresponding data in regard to the effects of the ochers, siennas, umbers, and metallic browns.

Ochers tend first to retard and then to accelerate the drying of the oil. The initial retardation is caused by the adsorption of the drier from the oil, the final acceleration is due to the formation of iron soaps which act as catalysts. The iron oxide in an ocher reacts less readily with the drying oil than does the ferric oxide in a red iron oxide pigment. Siennas and umbers show less effect on the initial rate of oxidation of the oil than does ocher because the removal of the lead drier is compensated by the formation of a small amount of manganese drier.

Procedure

The apparatus used and the procedure followed in determining the rate of oxidation of the oil were similar to those described by Rhodes and Van Wirt.[3] Two parts by weight of the pigment to be studied were mixed with three parts of the vehicle and the mixture was ground to a smooth paint. The vehicle used in each case consisted of raw linseed oil in which had been dissolved sufficient lead linoleate drier to contain an amount of lead equivalent to 0.2 per cent by weight of the oil. Each paint was allowed to age in a sealed container for at least 2 weeks before being tested. Weighted samples of the paint were then exposed to an atmosphere of pure oxygen at 30° C., and the rate of absorption of oxygen and the rate of evolution of volatile matter were measured. The rate of oxidation of the vehicle alone was determined in a similar manner. In each case at least two parallel determinations were made with each paint. The individual determinations gave results which agree with each other within the limits of experimental error.

Materials

The linseed oil used in this work was pure refined linseed oil from North American seed. It showed the following analysis:

Specific gravity at 15.5° C.	0.939
Refractive index at 25° C.	1.4788
Acid number	0.452
Saponification number	195.3
Iodine number	170.5

The analyses of the pigments used are shown by Table I.

Table I—Analyses of Pigments

Pigment	SiO_2	Fe_2O_3	Al_2O_3	CaO	MnO	CO_2	Combined H_2O	Free H_2O
White ocher	61.86	4.72	24.50	—	—	0.00	8.72	0.05
French ocher	53.77	18.86	17.95	—	—	0.10	9.54	0.23
Domestic ocher	46.72	22.79	18.79	—	—	0.02	10.68	0.47
Raw sienna	43.98	34.22	12.30	0.69	0.60	0.44	6.68	1.01
Burnt Italian sienna	19.40	69.90	3.55	—	0.50	0.08	6.00	1.54
Burnt American umber	20.14	54.14	9.41	1.27	4.72	0.34	8.21	1.87
Burnt Turkey umber	17.58	52.04	12.36	—	10.63	0.03	6.75	0.52
Metallic brown	14.15	75.50	6.10	—	—	0.03	1.83	0.66
Metallic brown	30.23	51.33	7.89	1.32	—	0.30	7.81	1.10

Results

The results are shown graphically by the accompanying curves, in which the amounts of oxygen absorbed and the amounts of volatile matter evolved (each expressed in terms of percentage by weight of the oil in the paint) are plotted against the lengths of time of exposure. For each pigment there is plotted only one curve, depicting the average results of two or more check determinations. On each diagram the graphs for the rate of absorption of oxygen and the rate of evolution of volatile matter for the vehicle alone are shown for purposes of comparison.

OCHERS (Figure 1)—Each of the ochers tested shows a marked effect in retarding the initial rate of oxidation of

[1] Received June 16, 1925.

[2] THIS JOURNAL, 16, 960 (1924).

[3] *Ibid.*, 15, 1135 (1923).

the oil. This initial retardation is probably caused by the adsorption of some of the lead drier by the pigment. The very finely divided French ocher shows a much more pronounced effect in delaying the oxidation than does the somewhat coarser domestic ocher. In order to determine whether or not these pigments do actually adsorb the drier from the vehicle, paints made from French ocher and from domestic ocher were centrifuged to separate the pigment and the

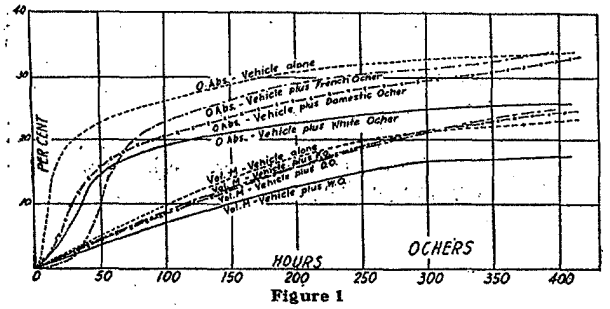

Figure 1

clear supernatant vehicle was analyzed for lead. A sample of the vehicle alone was also centrifuged to remove any suspended matter and the clarified oil was analyzed for lead. The results were as follows:

Pigment	Concentration of lead in centrifuged liquid Per cent
None	0.094
French ocher	Trace
Domestic ocher	0.019

These experiments prove that the pigments do actually remove lead drier by adsorption, and that the adsorption is more pronounced in the case of the French ocher. It does not follow, of course, that in a paint made with French ocher the lead drier is absolutely inert, since it is possible that lead linoleate adsorbed on the pigment particles may still catalyze the oxidation of the oil to some extent. It is reasonable to assume, however, that the adsorbed drier will be somewhat less effective than drier actually in solution in the oil.

Both the French ocher and the domestic ocher tend to increase the final rate of oxidation of the oil, so that the paints made from these pigments ultimately absorb more oxygen than does the vehicle without pigment. This effect of the ochers in increasing the final rate of oxidation is presumably due to the interaction of the iron oxide with the acidic substances produced during the drying of the oil, with the resulting formation of iron driers which act as catalysts in promoting the oxidation of linseed oil. The white ocher, which is really a clay containing very little iron oxide, does

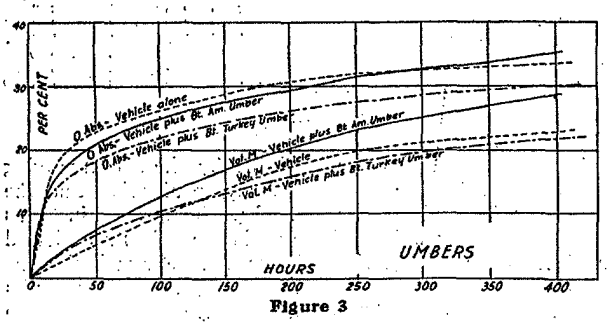

Figure 3

not show this effect of increasing the final rate of drying of the oil.

The ochers, however, accelerate the final drying of the oil to a lesser extent than do some of the iron oxide reds—as, for example, bright oxide and Tuscan red.[2] Many authorities explain the difference of color between the ochers and the reds by assuming that the ochers contain yellow ferric hydroxide whereas in the red pigments the iron is present as red ferric oxide. If this were true the red pigments would be less reactive than the ochers and would show less effect upon the rate of drying of the oil. The writers are inclined to ascribe the difference between the two types of pigments to the fact that the ferric oxide is strongly adsorbed in (or on)

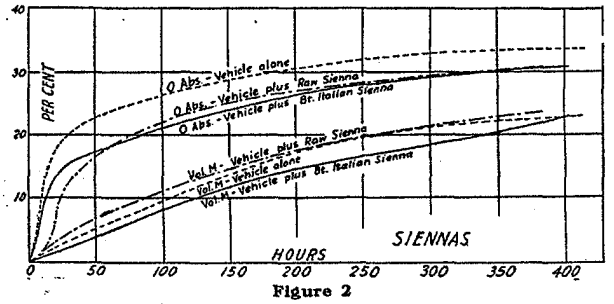

Figure 2

the particles of clay and therefore combines less readily with the acidic oxidation products of the oil.

Siennas (Figure 2)—In its effect upon the oxidation of linseed oil raw sienna behaves somewhat like domestic ocher. Burnt sienna, however, shows very little effect in decreasing the initial rate of oxidation of the oil. Experiments made to determine the extent to which lead drier is removed from linseed oil by adsorption on sienna pigments gave the following results:

Pigments	Concentration of lead in centrifuged liquid Per cent
None	0.094
Raw sienna	Trace
Burnt sienna	0.0049

The burnt sienna does not retard the initial rate of oxidation nearly so much as does domestic ocher, although the sienna adsorbs the lead drier more strongly than does the ocher, and raw sienna has less effect upon the rate of oxidation than has French ocher, although both pigments adsorb the drier almost completely. Apparently, the formation of small amounts of manganese drier from the manganese in the sienna tends largely to counteract the effect of the removal of the lead drier. That such manganese driers are formed is shown by the fact that the centrifuged vehicle from the sienna paints gives a distinct, although faint, test for manganese.

Umbers (Figure 3)—Neither burnt Turkey umber nor burnt American umber retards the initial rate of oxidation of the oil; in fact, both paints made with umber dried more rapidly than did the vehicle alone. This agrees with the

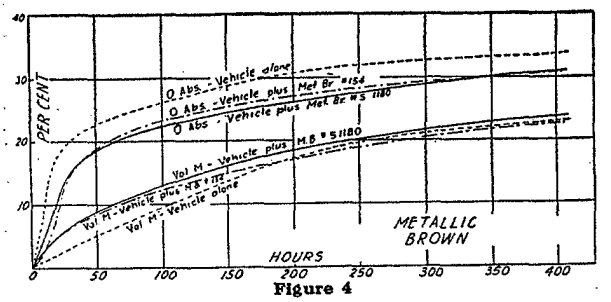

Figure 4

observation of Ingalls[4] that umber markedly increases the rate of drying of linseed oil.

Experiments made to determine the extent to which umber adsorbs the lead drier gave the following results:

[4] *Chem. Met. Eng.*, **22**, 590 (1920).

Pigments	Concentration of lead in centrifuged liquid Per cent
None	0.094
Burnt American umber	Faint trace

The centrifuged vehicle from the paint made with umber gave a distinct test for manganese. It is obvious that the failure of umber to retard the initial rate of oxidation of the oil is due to the formation of a small amount of manganese drier by the interaction of the oil and the pigment.

METALLIC BROWN (Figure 4)—Paints made from metallic brown as a pigment behave very much like paints made from domestic ocher, although both the decrease in the initial rate of oxidation and the increase in the final rate of oxidation are somewhat less pronounced.

Preparation of *l*-Arabinose from Mesquite Gum[1,2]

By Ernest Anderson and Lila Sands

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Arabinose is readily prepared by the hydrolysis of mesquite gum for 3 hours at 80° C. in six times its weight of 4 per cent sulfuric acid. After removal of the acid as barium sulfate the neutral solution is concentrated, the salts precipitated by alcohol, and the alcohol solution of the sugars concentrated and allowed to crystallize. The yield of crystalline sugar varies from 27 to 36 per cent of the gum used and the melting point varies from 140° to 155° C. This product can be recrystallized from water, mixtures of water and alcohol, and from glacial acetic acid. Mesquite gum can be purchased in large amounts in the Southwest.

THE preparation of *l*-arabinose from various plant products has frequently been described in the literature.[3] Browne[4] gives the general method followed in the preparation of the sugar. Lippmann,[5] Abderhalden[6] and Beilstein,[7] give reviews of the literature dealing with the preparation, together with numerous references. Hudson,[8] states that beet pulp is a better source of arabinose than cherry gum, which is usually recommended by textbooks. Harding[9] prepares arabinose by hydrolyzing beet pulp for 1.5 hours in a boiling 1 per cent solution of sulfuric acid and obtains from 4 to 5 per cent of the beet pulp in the form of arabinose.

The present investigation was undertaken in connection with the study of plant gums. The crude material, mesquite gum, has been found to give good yields of the *l*-arabinose when prepared by the following method.

Note—Mesquite gum is found on the mesquite tree, *Prosopis juliflora*, and other species of mesquite, through a great part of Texas, New Mexico, Arizona, and northern Mexico. The gum exudes from the stem and branches in irregular, roundish, or vermiform pieces of various sizes, usually small, weighing 5 grams or less, but sometimes weighing as much as 25 grams. When the gum first appears it is soft and sticky. At this stage it often runs down the branch. It gradually dries out and becomes hard and so brittle that it can be powdered in a mortar. This gum is collected by the Indians and Mexicans. It is carried by most of the drug stores of Tucson and with a few weeks' notice could be supplied in large amounts by the Martin Drug Co., of Tucson, at 30 cents or less per pound. Undoubtedly other chemical supply houses of the Southwest, such as the Mine & Smelter Supply Co., of El Paso, could secure large amounts of the gum. Mesquite gum is fully described in an article by Anderson, Sands, and Sturgis, *Am. J. Pharmacy*, **97**, 589 (1925).

Dissolve 500 grams of mesquite gum in 3 liters of water contained in a 5-liter flask. (If the mixture of mesquite gum and water is let stand for 10 hours and then shaken it will form a clear solution. The same result can be attained by heating the mixture in the boiling water bath for an hour with frequent stirring. The acid should not be added until the gum is dissolved.) To this solution add a cool solution of 125 grams of concentrated sulfuric acid in 70 cc. of water, and heat to 80° C. for 3 hours in a large water bath. Precipitate the sulfuric acid by adding to the hot solution, a hot concentrated solution of 410 grams crystalline barium hydroxide. (The barium hydroxide should not contain more than traces of carbonate or the solution will foam.) Adjust the solution to neutrality by adding small amounts of barium hydroxide solution or sulfuric acid solution as required. Let the barium sulfate settle, siphon the clear solution, filter the barium sulfate on a Büchner funnel, and wash it with hot water. Combine the solutions and concentrate in an evaporating dish on the boiling water bath, to a volume of approximately 650 cc. When the gum is hydrolyzed at 80° C. the water cannot be distilled off *in vacuo* because of foaming but must be evaporated in an open dish. Transfer the solution to a 3-liter flask. The total volume should be 700 cc. To this solution add with shaking 1.5 liters of 95 per cent ethyl alcohol. Let stand until the solution is no longer turbid. Decant the sugar solution from the gummy barium salts and extract the latter four times under the reflux, each time with 500 cc. of boiling methanol (prepared by distilling wood alcohol over quicklime). After the third extraction transfer the salt to an evaporating dish and grind to a powder. Concentrate the ethyl alcohol solution of the sugars *in vacuo* on the boiling water bath to a thin sirup. (If all the water is removed by heating the gum *in vacuo* for some time the sugar will not crystallize. Seeding with crystals of arabinose hastens crystallization.) Let this cool. After crystallization has begun add a small volume of ethyl alcohol, being careful not to precipitate an appreciable amount of gummy material. Set the solution in the refrigerator to

[1] Received June 24, 1925. Presented before the joint meeting of the Divisions of Organic Chemistry and Chemistry of Medicinal Products at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

[2] This is the first of a series of papers dealing with the chemistry of the plant gums in general and especially with those that occur in the southwestern part of the United States.

[3] Scheibler, *Ber.*, **1**, 58 (1869); **6**, 612 (1873); Allen and Tollens, *Ann.*, **260**, 289 (1890); Ullick, *Z. Zuckerind. u. Landw.*, **23**, 274 (1894); Marquardt and Schulz, *Z. Ver. deut. Zuckerind.*, **51**, 864 (1901); Bauer, *Ibid.*, **36**, 751 (1886); *J. prakt. Chem.*, **30**, 367 (1884); Kiliani, *Ber.*, **19**, 3029 (1886); Ruff and Meusser, *Ibid.*, **34**, 1364 (1901); Subaschow, *Z. Ver. deut. Zuckerind.*, **46**, 270 (1896); Tollens and Browne, *Ber.*, **35**, 1464 (1902); Tollens, *Z. angew. Chem.*, **20**, 477 (1902); Steiger and Schulze, *Ber.*, **23**, 3110 (1890); Schulze, *Z. physiol. Chem.*, **16**, 386 (1892); Wroblewski, *Ber.*, **30**, 2289 (1897); **31**, 1128 (1898); Yoshimura, *Chem. Zentr.*, **1896**, 46; Winterstein and Blau, *Z. physiol. Chem.*, **75**, 410 (1911); Power and Salway, *J. Chem. Soc. (London)*, **103**, 191 (1913); Kiliani and Koehler, *Ber.*, **37**, 1210 (1904); Houers and Tollens, *Ibid.*, **36**, 3306 (1903).

[4] Handbook of Sugar Analysis, **1912**, p. 548.

[5] "Chemie der Zuckerarten," Vol. I, 3rd ed., **1904**, p. 55.

[6] Biochemische Handlexikon, **1911**, Vol. II, pp. 21, 279; Vol. VIII, p. 112.

[7] Handbuch der Organischen Chemie, Vol. I, 4th ed., **1913**, p. 860.

[8] THIS JOURNAL, **10**, 177 (1918).

[9] *C. A.*, **17**, 1164 (1923).