clay at various steps is based entirely on the behavior of the retained samples.

Table II is an abstracted record of the work done by the clay after the various burnings. All the runs with clay of the same condition have been grouped together, and each column represents the total. The individual yield in barrels per ton varied only slightly in any case from the average for its group. The constants determined on the refined product for control—A. P. I. gravity, Engler end point, and color—are indicated by giving the highest and lowest of each in each group. The table also shows the gain in weight of the clay at each use, and the loss on burning.

Refining with Reburned Clay

The retained samples of clay from the various burnings were compared by refining with them the gasoline from a Fleming pressure distillate which was known to give a product of the desired characteristics with the unused clay, at about 450 barrels per ton in the glass apparatus. In running these tests, 11.5 grams of the clay were used in each case, 1220 cc. of the pressure distillate, which had a gasoline content of about 75 per cent, being charged. Table III shows the results obtained, as regards color, stability, and gumming tests, and gives for comparison the methylene blue numbers and turpentine temperature reaction.

From the above it is evident that, although there is a slight difference in the stability of the products from the burned clays as compared with that from the unburned, it is not large enough to be of practical importance, especially since reburnings after the first seem to leave the clay unaffected. There is, therefore, no reason to doubt that the reburning and re-use can be repeated practically indefinitely without further impairing the efficiency of the clay.

Table III—Comparison of Reburned Clays for Vapor-Phase Refining

		Reburned				
Clay used	Unused	Once	Twice	3 times	4 times	5 times
Methylene blue number	0.10	1.0	1.5	1.0	1.0	1.5
Turpentine temperature reaction, ° F.	148	6	12	4	5	6
Yield, barrels per ton[a]	456	461	461	460	456	467
Product, initial boiling point, ° F.	108	110	118	104	116	110
Temperature, ° F.:						
20% off	210	208	212	208	216	216
50% off	288	282	286	282	284	288
90% off	384	384	381	380	380	382
End point	416	410	422	414	414	426
Gum mg. per 100 cc.						
Copper dish	23.9	19.6	21.3	18.6	13.6	16.2
Glass dish	6	6	8	9	5	7
Color (Saybolt):						
Original	30	30	29	30	28	30
After 2 days (south light)	29	27	26	26	27	27
After 4 days (south light)	26	25	25	25	25	25
After 7 days (south light)	25	23	24	23	24	23

[a] A Fleming pressure distillate was used in performing these tests.

Conclusions

Organic material left in clay used for vapor-phase refining can be burned out sufficiently at a temperature of 1020° F. to allow of efficient re-use of the clay. This has been found to leave the efficiency of a Georgia fuller's earth entirely unimpaired by one reburning.

Reburned Florida clay, revivified at 1020° F., is only slightly less active than the unused clay. After the first reburning its utility remains unimpaired by further burnings as far as the present experiments have been carried—that is, through five reburnings.

Effect of Various Carbon Pigments upon Rate of Oxidation of Linseed Oil[1,2]

By F. H. Rhodes and H. E. Goldsmith

Cornell University, Ithaca, N. Y.

Lampblack and carbon black markedly inhibit the oxidation of raw linseed oil. This effect is not due to the presence of an oily impurity in the pigment, but is due largely to the adsorption on the pigment of the intermediate oxidation product which is the true catalyst in the drying of linseed oil. When added to linseed oil containing drier, the carbon pigments adsorb some of the drier and for this reason also tend to retard the drying. The extent to which the oxidation is inhibited varies with the nature of the drier present.

THE effect of the carbon pigments upon the rate of drying of paints has been discussed by numerous authorities. It is generally agreed[3,4,5] that some carbon pigments, particularly lampblack, act as "retarders in the drying of paints and tend to inhibit the oxidation of the oil. The exact cause of this effect is not fully understood. Several authorities[3,4,5,6] attribute the retarding action of lampblack to the presence in the pigment of a certain amount of oily material. In none of this previous work on the effect of black carbon pigments on the rate of drying of paints has a quantitative study been made of the effect of such pigments upon the rate of oxidation of linseed oil.

The present investigation was undertaken to determine quantitatively the effects of the black carbon pigments on the rate of oxidation of linseed oil, and to establish the causes for these observed effects.

Materials

Pure linseed oil from North American seed was used. It showed the following analysis:

Specific gravity at 15° C.	0.9315
Refractive index at 15° C.	1.4820
Acid number	4.51
Saponification number	195.3
Iodine number	170.5

The driers were linoleate paste driers, showing the following analyses:

Cobalt Paste Drier	
Cobalt (calcd. as metal)	5.74 per cent
Manganese	Trace
Magnesium, copper, nickel	Spectroscopic traces only

[1] Received January 19, 1926.

[2] This article is respectfully dedicated by the authors to Prof. L. M. Dennis, and will be reprinted as Article Number Two in the Louis Munroe Dennis Quarter Century Volume to be published in commemoration of the completion by Professor Dennis of twenty-five years of service as head of the Department of Chemistry at Cornell University.

[3] Toch, "Chemistry and Technology of Paints," 2nd ed., 1916, p. 99.

[4] Sabin, "Technology of Paint and Varnish," 2nd ed., 1916, p. 201.

[5] Hurst, "Painters' Colours, Oils and Varnishes," 2nd ed., 1901, p. 250.

[6] Morrell, "Rubber, Resins, Paints and Varnishes," 1920, p. 136.

Manganese Paste Drier	
Manganese (calcd. as metal)	5.16 per cent
Iron	0.055 per cent
Aluminum, copper, sodium	Spectroscopic traces only

Lead Paste Drier	
Lead (calcd. as metal)	17.59 per cent
Iron	0.0605 per cent
Sodium, aluminum, arsenic, magnesium, silicon	Spectroscopic traces only

In making up the vehicles for the paints studied, a calculated amount of the paste drier was dissolved in a known weight of warm linseed oil. The vehicles were stored in sealed bottles until used. The amounts of drier used were sufficient to give the following concentrations of active material (calculated as metal) in the vehicles:

Vehicle No.	Metal	Per cent
1	Lead	0.275
2	Manganese	0.0732
3	Cobalt	0.0221

The carbon pigments were:

	Carbon black Per cent	Lampblack Per cent	Vine black Per cent
Ash	0.166	0.2028	8.516
Moisture	3.68	2.15	5.72
Soluble in benzene	Trace	5.82	None

Procedure

The procedure was similar to that described by Rhodes and Van Wirt.[7] Paints prepared from pigment and linseed oil were 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. Unless otherwise specified, each paint contained one part by weight of pigment and nine parts by weight of vehicle. With each paint there were made at least two parallel determinations, giving results which agreed to within the limits of experimental error.

Results

The results are shown graphically by the accompanying charts, 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. A single curve is shown to represent the average results obtained in the two or more check determinations made with each sample.

Linseed Oil Alone

Chart I shows the rates of oxidation and the rates of evolution of volatile matter of raw linseed oil alone and of the mixtures of linseed oil with the various driers. The autocatalytic character of the reaction involved in the drying of linseed oil and the effects of the driers in accelerating the formation of the autocatalyst and thus increasing the initial rate of oxidation are clearly indicated.

Carbon Pigments Added

Chart II shows the results obtained in a series of experiments made to determine the rate of oxidation of paints made from raw linseed oil and carbon pigments. The addition of the carbon pigments markedly retarded the rate of oxidation of the oil. The paints were still somewhat tacky after 400 hours' exposure.

As a supplementary experiment, samples of carbon black paint and of linseed oil alone were painted in parallel strips on a glass plate and allowed to stand in the air at room temperature. The film of oil became tacky in 4 days and was dry to the touch in 7 days. The paint made from carbon black became tacky only after 22 days and was dry to the touch only after 28 days.

[7] This Journal, 15, 1135 (1923).

It has been stated that the oily impurities in lampblack are largely responsible for the action of this pigment in retarding the oxidation of linseed oil. In order to obtain further information as to the effect of oil-soluble impurities in the pigments, samples of paints made from carbon black and from lampblack were centrifuged and the rates of oxidation of the clarified oils thus obtained were determined. The linseed oil obtained from the carbon black paint was clear and of a lighter color than the original raw oil from which the paint had been prepared; the oil from the lampblack paint was dark red and somewhat fluorescent.

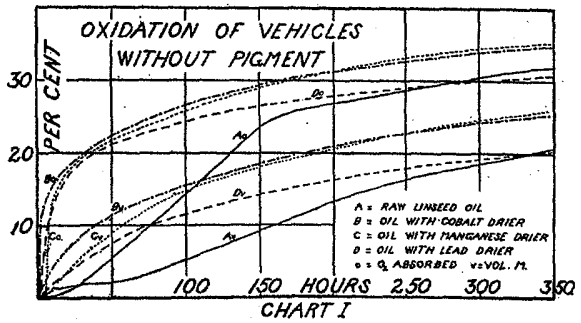

CHART I

The results of the oxidation experiments made with these oils are shown on Chart II. The oils separated from the paints oxidized a little more slowly at first than did the raw linseed oil, but after a short period of induction the separated oils took up oxygen at almost the same rate as did the fresh raw oil. These experiments prove that the effect of black carbon pigments in inhibiting the oxidation is not due to the presence in the pigment of impurities that are soluble in linseed oil. The action of the blacks in delaying the drying must, therefore, be due to some specific action of the pigments themselves. That the oils separated from the paints showed more marked periods of induction than fresh linseed oil suggests that the pigments may have adsorbed and removed the small amount of the autocatalytic intermediate oxidation product which is normally present in ordinary raw linseed oil. This, in turn, suggests that the slowness of drying of paints containing carbon pigments may be due to the fact that the pigments continuously adsorb and remove the autocatalyst as fast as it is formed.

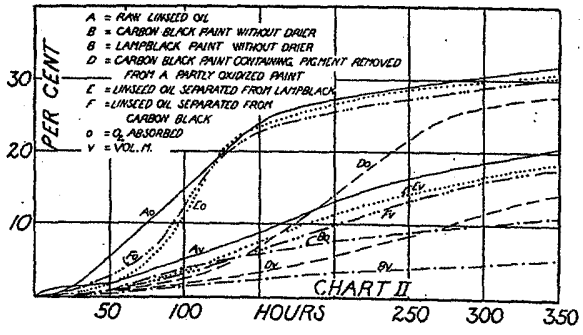

CHART II

Additional evidence in favor of this hypothesis is supplied by the following experiment: A paint made with carbon black was oxidized at 100° C. until it became thick when cooled. The pigment was separated from the vehicle by centrifuging, and was then washed with raw oil and again centrifuged to remove the wash oil. The resulting pigment was made up into a paint with raw linseed oil and the rate of oxidation of this paint was determined. Oxidation took

place very slowly for the first 150 hours, but after this period of induction oxygen was absorbed about as rapidly as by the raw oil alone. It will be observed that this paint made from pigment recovered from a partly oxidized paint dried much more rapidly than did paint made from the original pigment. The results indicate that during the preliminary treatment the carbon black had become almost saturated with the intermediate oxidation product, so that in the

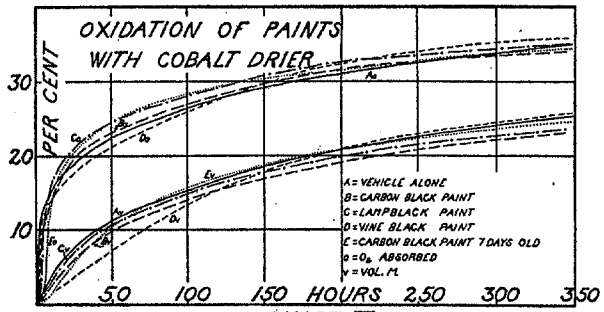

CHART III

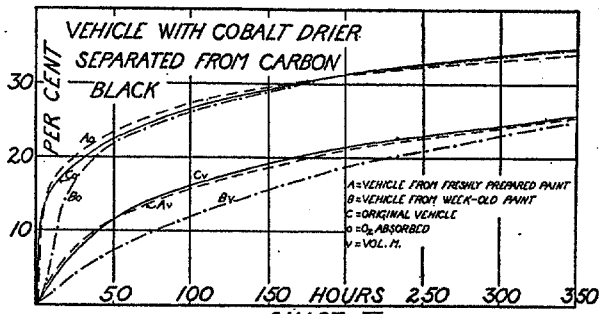

CHART IV

oxidation of the final paint complete saturation was attained in a short time, after which the autocatalyst remained in the oil to exert its normal effect in accelerating the drying.

Cobalt Drier

The effect of carbon pigments on the rate of oxidation of linseed oil in the presence of cobalt drier was next investigated. The paints were made up to contain 10 per cent of pigment suspended in linseed oil in which had been dissolved sufficient cobalt linoleate to contain an amount of cobalt equivalent to 0.0221 per cent of the weight of the oil. The results are shown by Chart III.

Curves III-B and III-C show the rates of oxidation of freshly prepared paints made from carbon black and from lampblack. These two curves are practically identical in form. In each case the presence of the pigment causes a very slight retardation of the initial rate of oxidation of the vehicle. In these experiments the effect of the pigments in inhibiting the oxidation of the oil was very much less than in the experiments made with paints prepared from linseed oil without drier. It appears that in the presence of the powerful cobalt drier the intermediate oxidation product that is the true catalyst in the oxidation reaction is formed much more rapidly than it is removed by adsorption on the pigment. Vine black (Curve III-D) had even less effect

being exposed to oxygen the initial rate of oxidation was appreciably less than the initial rate of oxidation of the freshly prepared paint. This appears to be due to the gradual adsorption of some of the cobalt drier by the pigment. In order to determine to what extent this adsorption of the drier occurs, freshly prepared and week-old samples of the carbon black paint were clarified by centrifuging and the resulting clear vehicles were analyzed for cobalt and tested to determine the rate of absorption of oxygen. The clarified vehicle from the freshly prepared paint contained 0.003 per cent of cobalt; that from the week-old paint contained only a trace of cobalt.

The rates of oxidation of the two clarified samples are shown by Chart IV. The clarified vehicle from the freshly made paint oxidized at almost exactly the same rate as did the original vehicle from which the paint was prepared. The vehicle recovered from the paint which had been allowed to stand for a week oxidized much more slowly. This was to be expected, since the concentration of drier in this sample was extremely low. From a comparison of Curves IV-B and IV-C it will be seen that the vehicle recovered from the week-old paint oxidized even more slowly than did the paint itself. It would appear that the cobalt drier still possesses some catalytic activity even when adsorbed in the pigment, although, of course, the adsorbed drier is less effective than drier in solution.

Lead Drier

In studying the effect of the pigments upon the rate of drying of linseed oil in the presence of lead drier, the vehicle used contained an amount of lead linoleate equivalent to 0.275 per cent of lead. The paints were made up to contain 10 per cent of pigment as before. The paint made

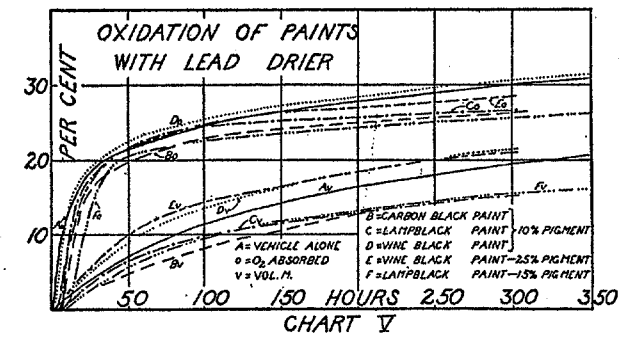

CHART V

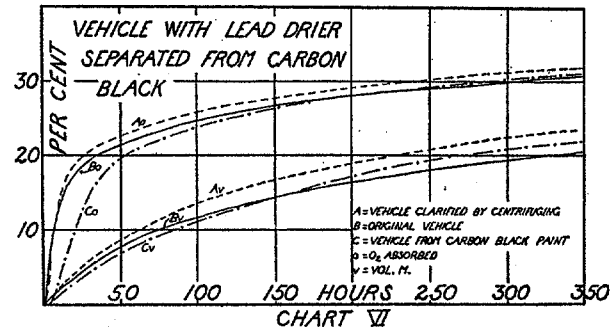

CHART VI

upon the initial rate of oxidation than had carbon black or lampblack. This is to be expected, since the vine black is relatively dense and gives relatively less adsorbing surface.

It was observed (Curve III-E) that when the carbon black paint was allowed to stand for several days before from carbon black absorbed no measurable amount of oxygen during the first 5 hours' exposure. Oxidation then began and, after a short period of induction, progressed normally. The paint made from lampblack showed about the same characteristics as did the paint made from carbon

black, although the length of time during which no oxygen was absorbed was somewhat longer.

The effect of the pigments in retarding the oxidation of the vehicle may be due in part to the adsorption of the drier by the pigment. To determine the extent to which such adsorption occurs, a sample of the carbon black paint was centrifuged and the resulting clarified vehicle was analyzed for lead. For comparison, an analysis was made on a portion of the original vehicle which had been similarly centrifuged to remove any drier not actually in solution. The clarified original vehicle contained 0.097 per cent of lead, while the vehicle recovered from the paint contained only 0.0312 per cent of lead. Obviously, the carbon black had adsorbed and removed over two-thirds of the drier present in actual solution in the oil.

The progress of the oxidation of these clarified vehicles is shown by Chart V. In spite of the fact that the lead content of the original vehicle was reduced from 0.275 per

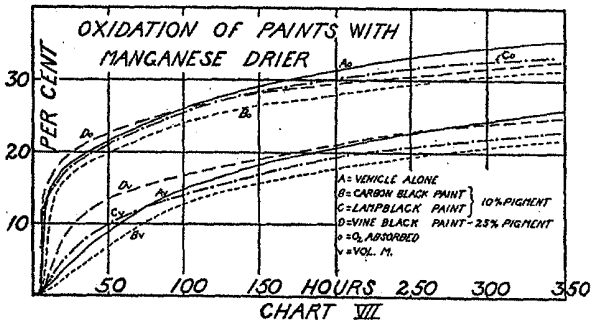

CHART VII

cent to 0.097 per cent by centrifuging, the centrifuged vehicle oxidized at almost exactly the same rate as did the original. These results indicate that, under certain conditions at least, only a portion of the lead linoleate added to linseed oil actually passes into solution in the oil, and that only the comparatively small amount of drier in actual solution is effective in promoting the drying of the oil. The vehicle which was separated from the paint, and which contained only 0.0312 per cent of lead, showed a more pronounced period of induction and an appreciably slower rate of oxidation than did the original vehicle. This is the logical result of the lower concentration of dissolved drier.

The adsorption of a large part of the lead drier by the pigment does not, however, explain all the phenomena observed in connection with the oxidation of the paints made with carbon black or lampblack. That practically no oxygen was taken up during the first few hours of exposure may be explained by the hypothesis that the pigment also adsorbed the small amount of autocatalyst which may have been present in the original oil or which may have been produced during this initial period. Only after several hours was sufficient unadsorbed autocatalyst produced to exert a marked effect in promoting the oxidation. It will be observed that in the case of the paint made up to contain 15 per cent of lampblack the initial period during which no oxidation took place was somewhat more pronounced than in the case of the paint containing only 10 per cent of lampblack. This is in agreement with the theory as outlined above.

That the effect of the pigment in inhibiting the oxidation continued for a few hours only instead of for many days, as in the case of the paint made from raw linseed oil, is due to the fact that in the present case the adsorption of the lead drier by the pigment very greatly decreased the adsorptive capacity of the pigment for the intermediate autocatalyst. It will be observed that in the case of the paints oxidation, when once started, took place somewhat more rapidly than in the case of the clarified vehicle separated from the paint (Chart VI). This provides additional indication that drier adsorbed on the pigment may still show some catalytic activity.

Paints made up to contain 10 per cent of vine black oxidized almost as rapidly as did the original vehicle. When the concentration of the vine black was increased to 25 per cent, a somewhat more pronounced effect was noted. That vine black is much less effective than carbon black or lampblack in retarding the drying of the oil is due, of course, to the smaller adsorptive power of the vine black.

Manganese Drier

Finally, the effects of carbon pigments upon the drying of the vehicle containing manganese drier were studied (Chart VII). The vehicle contained 0.0732 per cent of manganese. The lampblack and carbon black paints contained 10 per cent by weight of pigment; the vine black paint was made up to contain 25 per cent by weight of pigment. In no case did the presence of the pigment appear to have much influence upon the rate of oxidation of the linseed oil, although the paint made with carbon black showed a slightly longer period of induction than did the vehicle alone.

To determine to what extent the pigment absorbs and removes the manganese drier, samples of the original vehicle and of the carbon black paint were clarified by centrifuging. The centrifuged vehicle contained 0.0262 per cent of manganese, while the vehicle recovered from the paint contained only 0.0065 per cent. The rates of oxidation of the clarified vehicle and of the vehicle recovered from the paint were substantially the same as that of the original vehicle (Chart VIII).

Conclusions

1—The addition of lampblack or carbon black to raw linseed oil very markedly inhibits the oxidation of the oil.

2—The effect of the carbon pigments in inhibiting the oxidation of linseed oil is not due to the presence of oily or oil-soluble impurities in the pigments.

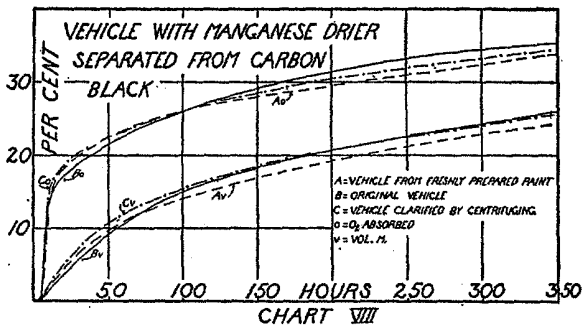

CHART VIII

3—The effect of the carbon pigments in delaying the oxidation of raw linseed oil is due to the continuous adsorption of the intermediate oxidation product which acts as the true catalyst in the drying reaction.

4—The carbon pigments only slightly retard the oxidation of freshly prepared paints containing cobalt drier. The inhibiting effect becomes more pronounced as the paints are allowed to stand. This is due to the gradual adsorption of the cobalt drier by the pigment.

5—When added to linseed oil containing lead drier, carbon

black and lampblack almost completely inhibit the oxidation of the oil during the first few hours of exposure. This effect is due to the fact that the pigments adsorb not only a portion of the lead drier but also the small amount of autocatalytic oxidation product that is formed at the beginning of the oxidation.

6—Carbon pigments have little effect upon the rate of oxidation of linseed oil containing manganese drier.

Heterogeneous Catalysis[1]

III—Hydrogenation of Cottonseed Oil with Platinum

By A. S. Richardson and A. O. Snoddy

THE PROCTER & GAMBLE CO., IVORYDALE, OHIO

THE glycerides of cottonseed oil are derived from linoleic acid, oleic acid, and solid saturated acids, chiefly palmitic. Hydrogenation of such an oil may conceivably involve any combination of the following three changes: (1) linoleic to oleic acid; (2) oleic to stearic acid; (3) linoleic to stearic acid. The problem of the distribution of the total hydrogenation of cottonseed oil among these three changes belongs to a general field of investigation which has appropriately been described by various investigators as the problem of "selective hydrogenation."

The previous literature on the selective hydrogenation of fatty oils has been reviewed in the earlier papers of this series.[2] The present paper deals with the selective action of platinum black in the hydrogenation of cottonseed oil, but before proceeding to a discussion of the experimental data involved it will be in order to correct a rather widespread misunderstanding of the fundamental purpose of hydrogenation.

The predominating importance of selective hydrogenation in industry is pointed out. The hydrogenation of cottonseed oil with platinum catalyst has been investigated at temperatures varying from 40° to 240° C. The preferential conversion of linoleic acid to the oleic acid stage and also the formation of solid unsaturated acid is favored by increasing temperature over practically the whole of the range investigated. Hydrogenation of cottonseed oil with platinum catalyst does not appear to be so selective as with nickel catalyst.

Practical Importance of Selective Hydrogenation

Contrary to the impression which the casual reader may gain from a survey of the published papers on selective hydrogenation of oils, the subject is not primarily a theoretical one. It is a subject in which practical development on a large scale preceded any scientific literature.

The pioneers[3] in the field of hydrogenation of oils regarded their process merely as a means of converting liquid unsaturated to solid saturated fatty acids—for example, oleic or linoleic to stearic acid. As long as that idea prevailed in industry, hydrogenation was making important but comparatively slow progress. The chief impetus to industrial development was the discovery by Burchenal[4] that hydrogenation could be controlled so as to produce a product especially suited for edible purposes, in which the principal chemical change is the selective conversion of the highly unsaturated linoleic acid to the less unsaturated oleic acid, with the formation of relatively little stearic acid.

The mere fact that the average cottonseed oil is about 75 per cent derived from liquid fatty acids has never been a serious handicap to its use in edible fat. The average edible fat should and does contain a substantial excess of liquid constituents. However, the fact that about 65 per cent of this liquid fatty acid consists of linoleic acid renders cottonseed oil extremely susceptible to oxidation and resulting rancidity. Hence the possibility of converting linoleic to the relatively stable oleic acid by selective hydrogenation was even more attractive to the far-sighted manufacturer than the formation of solid saturated from unsaturated acid.

Burchenal's discovery was followed, in turn, by industrial development and by a series of investigations which show that hydrogenation inherently tends to be selective, but not completely so. Many conditions in practice may interfere with or defeat the purpose of selective hydrogenation. If this were not so, it is almost inconceivable that selective features of hydrogenation should have so long been unnoticed.

The most important factor to be controlled is the end point of hydrogenation. For instance, at a more or less well-defined critical point hydrogenation of vegetable oil containing linolein ceases to involve primarily the conversion of linolein to olein and results in substantial increase of stearin content. Carried beyond that point, hydrogenation becomes effectively less selective. Operating conditions may also render the process of hydrogenation effectively nonselective. For instance, unhydrogenated oil may be swept through the system into the finished product. This is particularly likely to occur in a continuous process, but may also occur in a batch process in which pockets of unhydrogenated oil persist throughout the reaction period as a result of incomplete agitation.

Temperature, perhaps, is the most important factor which has been shown to affect the inherent selective tendency of hydrogenation of oils in the presence of nickel catalyst. Moore, Richter, and Van Arsdel[5] found that the selective conversion of linolein to olein was favored by increasing temperature in the hydrogenation of cottonseed oil. Richardson, Knuth, and Milligan[2] have made the same observations on several oils in the temperature range 150° to 200° C., but have obtained conflicting results above 200° C.

Scope of Present Work

The present work was undertaken at the suggestion of H. J. Morrison for the immediate purpose of extending the

[1] Presented as a part of the Symposium on Cotton and Its Products and Vegetable Oils before the joint session of the Divisions of Agricultural and Food Chemistry, Biological, Cellulose, and Industrial and Engineering Chemistry at the 71st Meeting of the American Chemical Society, Tulsa, Okla., April 5 to 9, 1926.

[2] Richardson, Knuth, and Milligan, THIS JOURNAL, **16**, 519 (1924); **17**, 80 (1925).

[3] Leprince and Sieveke, German Patent 141,029 (August 14, 1902); Normann, British Patent 1515 (January 21, 1903).

[4] U. S. Patent 1,135,351 (application filed November 10, 1910, patent granted April 13, 1915).

[5] THIS JOURNAL, **9**, 451 (1917).