ity when exposed to light than the one having a peroxide value of 68.

The data given in Table IV show further that the four samples fresh from the refrigerator exposed to light at different times acquired nearly the same peroxide value before they became rancid. Also, the difference between the peroxide value of the previously protected samples at the time they were exposed to light and the peroxide value at the time they became rancid is strikingly near the peroxide value of the fresh refrigerator samples when they had become rancid.

This seems to suggest that the "compound" capable of becoming rancid remained unchanged during the time the oil was protected from harmful wavelengths of light, regardless of peroxide formation. On exposure of the oil to light the "compound" became susceptible to photochemical action leading to the development of rancidity.

It appears, therefore, that the normal induction period of an oil is influenced largely by the length of exposure and intensity of the light to which the oil has been subjected. The results obtained also indicate strikingly that the "compound" capable of becoming rancid is not so much affected by the development of peroxide as by exposure to light.

It is quite likely that different samples of the same kind of oil vary in their induction period because during the process of manufacture and marketing they have been exposed to different intensities of light for different lengths of time. Lea[1] has shown that once an oil or fat has been exposed to light for even a short period, placing it afterwards in the dark will not stop the development of rancidity. If an oil has had adequate protection from light the peroxide value developed at room temperature should not be given too great weight in estimating its induction period, for it is apparent that the induction period really begins when the oil is first exposed to light, irrespective of its peroxide value, and ends when the oil gives an organoleptic test for rancidity. The length of the induction period is also dependent to a greater degree than has been recognized heretofore upon the amount of light previously absorbed. Consequently protection from light is a potent means for extending the usual period during which an oil remains fresh.

Conclusions

1. The induction period of an oil is appreciably lengthened when the oil is kept in the dark, and it is likewise lengthened when oils are protected from light by a green wrapper delimited by 4,900 to 5,800 Ångström units.

2. An oil which has been protected from light for a certain period and then exposed to light will develop rancidity in about the same time as will a fresh sample of the same oil exposed to light under the same conditions.

3. The development of peroxides in oils protected from light by means of a green wrapper is no indication of the rate at which rancidity will develop in unprotected oils. The idea heretofore held that the time required for rancidity to develop is associated with the peroxide value is no longer tenable, except in the case of accelerated tests.

4. The results indicate that rancidity of an oil has no necessary correlation with the development of peroxides.

5. A high peroxide value in an oil does not mean that the induction period will be short. This is especially true if the oil has been adequately protected from light.

6. The time required for an oil which has been protected from light to become rancid is, under like conditions, the same regardless of the acquired peroxide value.

7. There is apparently a relationship (see Table IV) between the numerical increase in the peroxide value of an oil previously protected from the time it is exposed to light until it becomes rancid and the peroxide value of a fresh sample of the same oil when it becomes rancid.

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[1] Effect of light on Oxidation of Fats. Lea, Colin H. Proc. Roy. Soc. (London), B 108, page 175-89 (1931).

OIL RESISTANT PROTECTIVE COATINGS

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IN the storing and packaging of fats and oils there has long been a desire to procure an effective coating composition which would resist the penetration and be proof against the action of these substances. There are of course a number of products which are more or less suitable for this purpose, but nearly all of these possess one or more shortcomings. Relatively short useful life and high cost are the more prominent ones.

There are a number of substances, both inorganic and organic which have been used for this purpose; a variety of conditions dominating the choice as to when and where to use them. In this presentation we are particularly concerned with those types of products which will form a continuous non-porous or impervious adherent film on the container surface. The primary role played by these compositions is as a protector of the fat or oil, or the products containing same. If the material from which the container is made is metal or similar impervious substance, then the coating composition serves only to prevent any possible reaction which may take place between oil and the container material. However, if the material from which the container is made is more or less porous, includes non-liquid tight joints and is of relatively low mechanical strength, then there is required of the coating composition the task of remedying these shortcomings, as well as a retaining oil impervious film. These conditions prevail to varying degrees in the use of wooden barrels and fibre cartons. In the case of wooden barrels these compositions seal the pores of the wood as well as the joints between the pieces used in the construction of same, but do not directly add to the strength of same. With fibre cartons, however, the coating composition seals the pores of the fibre board, fills the crevices and strengthens the joints. It also stiffens the fibre material from which the carton is made. In addition, it leaves a smooth impervious film lining the inside of the container.

PROPERTIES REQUIRED

The requirements for products functioning as protective coatings are that they:

1. Have the property of forming continuous oil impervious films.
2. That they neither react nor are soluble in the oil that they contain.
3. That they give neither odor, flavor nor color to the oil.
4. That the film possesses satisfactory adhesion to the container surface for the prescribed time.
5. That the composition be proof against organic decay.
6. That the composition must be applied readily and with standard equipment.
7. That it must harden in a short period of time.
8. That the film must not develop brittleness at low temperatures and low humidities.
9. That its shrinkage factor should not be such as to result in checks and cracks rendering the coating useless.
10. That the cost must be such as to permit of its extensive use.

While these specifications seem rigid, they are very close to being achieved. In fact, for lining coatings for wooden containers this goal has almost been realized, while in the case of the fibre cartons there remains considerably more development work yet to be done. This is especially true with reference to the multi-piece container, as well as certain types of fibre board used in this type of construction.

Probably the most extensively used inorganic material for this purpose is sodium silicate of the 40°Be. form. Its use, however, is largely restricted to wooden containers, because of the brittleness which it develops, the disintergrating effect of the atmosphere, and its strong alkalinity. Its use will continue until a better competitive product becomes available at a price reasonably approximating the market value of sodium silicate.

TYPES OF SUBSTANCES USED

Among the organic compounds one is limited to those substances which are insoluble in and unaffected by oils and fats. These products consist of certain of the carbohydrates and proteins. Among the carbohydrates, the starches and starch derivatives find most extensive use because of their low cost. The carbohydrate gums, pentosans and related products found in nature are almost as low in price, and for certain uses definitely superior. The cellulose derivatives are probably the preferred products for this purpose, but because of their high cost find limited use. Among the proteins the glues probably find the broadest scope of use, certain applications requiring gelatin. To a considerably lesser degree casein and albumen are adaptable as well as the alginates, though the disadvantages of their use undoubtedly outshadow their possible advantages.

Whatever the substances used for this purpose, it is invariably good practice to compound with same, a variety of addition products to modify the properties possessed by these materials, and at the same time contribute desirable elements adapting these products to their specific uses. An agent which would prevent the embrittling of the film due to age or the drying out of same is frequently added. To the carbohydrate films such as the starches, the plasticizing agents consist essentially of glycerol and the glycols, while the proteins may be softened or rendered flexible by these same substances, as well as sulphonated oils, more particularly castor which serves effectively for this purpose. The other additive is the preservative which inhibits organic decay. Considerable care must be exercised in the selection of these preservatives, in order to avoid affecting the taste, odor and color the oil. Boric acid and the borates are effective only when used in large amounts. The aromatic alcohols as well as the terpene alcohols are effective when used in relatively small amounts, but nearly all of them, even in small amounts, transmit odor and/or taste to the oil. The alkali salts of the aromatic acids, while less effective, do not possess the above faults. Sodium salicylate is representative of this group. Even with the use of these preservatives there is still much to be desired, as they are far from adequate as inhibitors of decay in humid and warm climatic conditions, when such proteins as glue, casein and albumen are used. Development work is now under way which may evolve more effective preservatives for this purpose. While the above referred to substances plasticize the films, their hygroscopicity is their most conspicuous drawback. This is particularly the case with glycerol and the glycols, and results in brittle films which develop cracks when low relative humidities are sustained for long periods of time.

METHODS OF APPLICATION

Water solutions of these various products are prepared, and after the plasticizer and preservative have been added, they are then ready for use. Because of the low cost and speed of application required, automatic spraying equipment finds most extensive use. Several concerns have developed and are merchandising automatic spray coating equipment for both barrels and fibre cartons. Brush application, because of its slow speed and uncertainty of complete coverage is ruled out because of high cost, except for the preparation of samples. Several forms of equipment involve the flowing or pouring operation to coat these containers. The outside of the container can of course be coated by a printing operation. Two separate coats or applications are far superior to a single coat job, even though the single application be a heavy one. The initial coat must be permitted to dry before applying the second coat, if best results are expected.

CONTAINER CONSTRUCTION

With the rapid expansion of factory packaged goods in small parcels, there came the demand for a container lower in price than the tin can. For the packaging of oils and fats many serious difficulties arose. One was the proper type of oilproof coating composition, and another a satisfactory fibre container construction with particular reference to the design of the joints. The transition from the tin can to the fibre carton includes the intermediate stage or hybrid: the part tin and part fibre container. This type was evolved to overcome the two troublesome problems of the all fibre carton, viz, the replacable cover, and the ability to produce leak tight joints at the chimes.

REPRESENTATIVE FORMULAS

Among the very low priced oilproof coating compositions which have been developed and tested, we found that a properly cooked alkali treated starch gave excellent results for a normal period of shelf life for merchandise consisting of or containing fats and oils. A working formula (and its cost) was made up as follows:

Starch	65%	@	3.0c lb.	—1.95c
Sodium silicate....	15%	@	1.7c lb.	—0.25c
Molasses	20%	@	1.0c lb.	—0.20c
Sodium salicylate..	0.4%	@	45.0c lb.	—0.18c
Total material cost per lb.........				2.58c

Water—by weight 10 times the above total.

PREPARATION OF COATING COMPOSITION

The sodium silicate is mixed with the water and then the starch is added. Any form of starch may be used, though the root starches such as potato and cassava are preferable to the cereal starches like corn and rice. This mixture is heated in a water jacket to the bursting of the starch granules, which will take place at about 165° F., and the mass is kept heated at this temperature or not exceeding 190° F. until the plastic clarifies, which may require about a half hour.

FUNCTIONS OF INGREDIENTS

The sodium silicate fills two roles: it provides the necessary alkalinity for the starch cook which results in a film of the desired adhesive properties, and at the same time provides an ultimate film less previous to oils for a longer period of time. As most starches have a pH value of 5 to 6, much of this alkalinity is destroyed in the cooking operation.

The molasses not only reduces the oil transmissibility of the dried film, but acts as a plasticizer or flexibilizing agent for the film. This property of the molasses is due in part to its hygroscopicity. The sodium salicylate is used as the preserving agent for both the starch and the molasses.

This composition has a covering capacity of 145 sq. ft. per pound of the total ingredients other than water and forms a film 1/1000 inch thick on an impervious surface. Its coverage on porous surfaces will naturally depend on the degree of porosity and the concentration of solids or amount of water used to thin out the composition. As the average quart size of fibre container has an inner area to be coated of from ½ sq. ft. to ¾ sq. ft., these cartons can then be coated with this composition at a material cost of from 9c to 14c per 1,000 cartons.

It is of course possible to improve upon this composition which will result in greater shelf life of oil imperviousness. This is achieved by using a gelatin or good grade of glue and plasticizing same with glycerol. However, this type of composition will cost several times that described above.

OTHER TYPES

If one desires still longer resistance to oil penetration, then the two-lamination coating compositions are preferred. This procedure consists in applying just a coating of the plasticized glare composition referred to above, and then coating this with a cellulose derivative lacquer such as cellulose nitrate, or cellulose acetate properly plasticized and formulated. These composite or laminated coatings are both water and oil proof. Such treatments involve a cost of many times that of the initial composition discussed.

METHODS OF TESTING

While many forms of accelerated tests have been proposed and tried, they appear to be far from producing the type of information desired. As a result the preferred form of test is to apply the coating composition, reproduce the expected amount of handling, and allow to stand for an indefinite period making frequent observations during that time, and noting the first signs of oil penetration. Though not conclusive, information of much value can be obtained from some forms of accelerated tests. The penetrating capacity of oils and fats can be very considerably increased by reducing the viscosity through the addition of substantial amounts of petroleum hydrocarbons from solvent naphthas to heavy distillates. Penetration and early failure are further hastened by the addition of small amounts of sulfonated oils such as castor and other "wetting agents" like the sodium sulfate esters of the higher fatty alcohols. These products are sold under such trade names as Igepon of the I. G., and General Dyestuffs Corp., and the Gardenols and Duponols of E. du Pont de Nemours.

Early detection of the failure of the protective film can be made more visible by dusting a very small amount of an oil soluble dyestuff on one or both sides of the fibre board before applying the coating composition. "Oil Red O" made by National Aniline and Chemical Co., serves this purpose excellently. It may also be dissolved in the oil mixture instead of being applied to the fibre board. While it is preferable to test the coating composition as applied to the fabricated container, in order to determine its value in sealing the joints in the side walls and chimes; tests may also be made on flat board by sealing with clay or paraffine wax a 1 inch glass tube on the surface to be tested. This method has the advantage of producing a pressure head which may be controlled by the heighth of the oil column in the glass tube.

TREND OF DEVELOPMENT

As previously pointed out there is still much to be done toward a more satisfactory coating composition. Whenever such a product is available at a reasonable price the fibre container will make deep inroads in the small parcel field for this type of material now using the tin can. Many of the products referred to will still be used, but their properties will be greatly improved through the use of an effective plasticizing agent which is non-hygroscopic. This element is by far the greatest handicap in the successful use of the water soluble coating compositions.

Several of the newer modifications of the various types of resins offer much promise, this is especially true of the Vinylites as produced by the Carbide & Carbon Chemicals Corp. Related products are being offered in other forms of resins including the Glyceryl-Phthalates, Formaldehyde-Ureas, and Phenol-Aldehydes, as well as specially treated Tung Oils and Tung Oil Resin varnishes. Doubtlessly, improvements on these forms as well as additional types will appear on the market from time to time.