UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH ADMINISTRATION
BUREAU OF ANIMAL INDUSTRY
WASHINGTON 25, D. C.

ADDRESS REPLY TO
"CHIEF OF BUREAU OF ANIMAL INDUSTRY"
AND REFER TO

YLY-9.136.2

August 3, 1949

640

Dr. William E. McCormick
Department of Industrial
Hygiene and Toxicology
The B. F. Goodrich Company
Akron, Ohio

Dear Dr. McCormick:

This is in reply to your letter of June 23rd requesting approval of your plastic wrapping films 012212 and 012220G for contact with meat and meat food products.

No objection will be made by this office to the use of your films as wrappers for federally inspected meat and meat food products, provided the extractables are composed, as you state, of monoglycerol oleate and acrawax.

We would appreciate receiving a copy of the method used by your laboratory in determining that chlorine and nitrogen were absent in the material extracted by petroleum ether.

Very truly yours,

R. M. Mehurin

R. M. Mehurin, Chief
Laboratory Section
Meat Inspection Division

20466001

BFG03566

August 23, 1949

Mr. R. M. Mehurin, Chief
Laboratory Section
Meat Inspection Division
U.S. Department of Agriculture
Washington, D.C.

Dear Mr. Mehurin:

In reply to your request of August 3, 1949 the following is a resume of the method which we used for determining the absence of both chloride and nitrogen in our plastic wrapping films 012212 and 012220G:

The Petroleum ether used for extracting the film should have a 30° - 60° C. boiling range.

Place small piece of sodium in 5cc test tube, being careful not to handle the test tube with the hands. Melt and drop in small piece of the sample, heat to redness, drop in another piece of the sample, heat to redness, etc. until no longer able to get "flash" of sample. Drop hot test tube into large test tube containing distilled water. (This should shatter.) Dissolve sample and filter.

Acidify 2 cc of the filtrate with dilute 6 normal nitric acid. Add a few drops of 5% silver nitrate. A white precipitate of silver chloride indicates chloride.

To 5cc of the sample add 5 drops each of 10% sodium hydroxide solution, 4% ferrous ammonium sulfate solution and 20% potassium fluoride solution. Boil gently 30 seconds. Cool under tap. Add one drop ferric chloride (5% solution). Acidify with dilute sulfuric acid (6 normal - 50% distilled water and 50% sulfuric acid) until ferric hydroxide just dissolves. Prussian blue indicates nitrogen.

Very truly yours,

Wm. E. McCormick
Department of Industrial
Hygiene and Toxicology

WEM
vs

20466002

June 23, 1949

Mr. R. M. Mehurin, Chief
Laboratory Section
Meat Inspection Division
U.S. Department of Agriculture
Washington, D.C.

Dear Mr. Mehurin:

It was agreed in our last conference on March 23, 1949 with you and Dr. Lehman's group that we would attempt to further characterize the nature of the extractables of films 012212 and 0122200, as presented in our report of February 24, 1949 (sent with my letter of March 4, 1949).

Samples of each of these films have been extracted with petroleum ether as outlined in the original report. These extracts were then subjected to both a standard sodium fusion-silver nitrate test for chloride and a standard sodium fusion-Prussian Blue test for nitrogen. The tests were negative in both cases. We believe this demonstrates quite well that the extractable are composed of monoglycerol oleate and acrawax as expressed to you in our conference.

We believe we have demonstrated the non-toxicity of each of these films for food packaging purposes. We, therefore, request that they be approved by your department as wrappers for meat or meat products.

Very truly yours,

Wm. E. McCormick
Department of Industrial
Hygiene and Toxicology

WEM
vs

A STUDY OF THE SOLUBILITY PROPERTIES OF TWO CAST FILMS FOR FOOD PACKAGING PURPOSES

BY THE B.F.GOODRICH COMPANY

Problem:

To study the solubility of two food wrapping films in both lard oil and dilute lactic acid (ph 4.0) and to appraise them with respect to the potential extraction of harmful ingredients in food for which they may serve as a wrapper.

Conclusions:

The data obtained showed that - (1) The maximum solubility of the polymer in the films when immersed in lard oil or dilute lactic acid was of the order of 38 milligrams per pound of extractant, or about 82 parts per million. (2) The maximum hydrogen cyanide concentration resulting from immersion in either lard oil or dilute lactic acid was no more then 0.25 p.p.m. This is equivalent to no more then about 0.1 milligrams per pound of food. (3) The maximum acrylonitrile content found with either lard oil or dilute lactic acid extraction was 2.5 p.p.m., equivalent to about 1.3 milligrams per pound of food.

The above figures represent maximum values which would obtain in practice only under the most adverse conditions.

Introduction:

The food wrappers in question are two semi transparent films manufactured by The B. F. Goodrich Company. They are designated as 012212 film and 012220G film. The extraction studies were designed in accordance with suggestions made by the Meat Inspection Division of The U.S. Department of Agriculture and were intended to provide information relative to the solubility of each of the films in both lard oil and dilute lactic acid solution and to determine the presence of any free hydrogen cyanide and monomeric acrylonitrile in these media. A representative sample of each of the films is attached with this report. The extraction studies were performed by placing the film samples in intimate contact with the two media for thirty days at a temperature of 100° F.

The determination of small amounts of soluble polymer in lard oil is a difficult

procedure. A turbidimetric method has been used by workers at Battelle Memorial Institute and while the technique has its merits, it determines the solubility only under a given set of conditions which may not apply in the present case. Qualitative use of this technique has been applied in this problem, but a different approach has been used for quantitative determination of polymer solubility.

It has been demonstrated that using chlorine or nitrogen atoms in the polymer as tracers is entirely impractical if not impossible unless the solubility is high. Since the solubility is definitely low, another technique was devised. Petroleum ether is essentially a non-solvent for the polymer films and an excellent solvent for lard oil. It is postulated that if there is no solubility of the polymer itself in lard oil, there will be no difference between the percent loss in weight of a film sample immersed in lard oil and subsequently extracted with petroleum ether and that of another film sample extracted only with petroleum ether. The only case which would lead to erroneous results is the case where a portion of the polymer itself is at least as soluble in lard oil as in petroleum ether. To guard against a false conclusion under such conditions, some knowledge of the non-polymer ingredients and their solubilities must exist. The difference between the percentage of film ingredients known to be soluble in lard oil or petroleum ether and the total percentage extracted by lard oil and petroleum ether is a measure of the maximum possible polymer solubility in the lard oil. A more probable value is the difference between the lard oil-petroleum ether extract and the petroleum ether extract alone. Even this value may give a value for polymer solubility which is too high because of solubility of a film ingredient in lard oil but not in petroleum ether. The procedure described below is based on the above postulates.

The method of determination of free monomeric acrylonitrile used in this study again gives the maximum possible value since it is based on determination of total nitrogen compounds volatile from lard oil or water and soluble in sulfuric acid to form an amide or ammonium salts. Thus it could include volatile amines, etc.

The method described for determination of free hydrogen cyanide has been reported

in the literature and was modified to suit the needs of this study and tested with known mixtures.

It has been found by experiment that approximately 3 grams of film will be used to wrap a pound package of oleomargarine or animal fat. In the conclusions as well as in the experimental data a value of 3 grams has been used as the weight of film needed per pound of fat.

Procedure:

Preliminary experimentation revealed no heat loss when drying these films at 105° C. Consequently the films were tested without first drying them to constant weight.

From a practical standpoint it was necessary to limit both the size of the film and the volume of immersion liquid while still maintaining essentially complete contact of the film with the liquid. Since about 3 grams of the film are used per pound of oleomargarine or animal fat, this ratio was first considered. However, it was later decided, after a discussion with the Meat Inspection Division, to use about 1 gram of film in 50 to 100 ml. of solvent. This ratio worked satisfactorily when a glass stoppered 250 ml. flask was used as the container, although the unsupported film was rather difficult to manipulate.

The following procedure was adopted for the immersion test:

Weigh a film, about 3" x 8", dried to constant weight. Place this in a 250-300 ml. glass stoppered flask containing 75 ml. of lard oil or of lactic acid water solution of pH 4. Work the sample around in the flask with a stirring rod until air bubbles are removed and maximum contact with the solvent is obtained, being especially sure that the sample is completely immersed. Place flask in an oven set for 100° F and allow it to reach oven temperature. Stopper and seal well with Pyseal. There should also be a liquid seal between stopper and flask, but do not use grease. Replace flask in oven for 30 days. Remove from oven and leave unopened until the analyses can be started.

The lard oil used was Eimer and Amend, Lard Oil, White, but it was definitely yellow brown in color and contained some suspended matter which dissolved or melted at 100° F or at higher temperatures leaving a clear deep straw colored liquid. Six samples of the film were immersed in each solvent.

At the completion of the immersion period the following analyses were made on the films and solutions:

A. Method of Analysis for Monomeric Acrylonitrile

Immediately upon opening the flask, pour 30 ml. of the solvent into the pear shaped flask which is connected to the condenser as shown in Figure I. This apparatus should be ready to operate before sampling. The two absorption tubes each contain 1 ml. of conc. H_2SO_4 and the ground glass joints are wet with the acid. Other joints may be sealed with stopcock grease. Bubble a stream of tank nitrogen or hydrogen through the system at a rate of 75-100 ml. per minute for 1 hour while keeping the sample flask near 100° C by means of a water bath.

At the end of this period, carefully wash the connecting tubes and the absorption tubes into a well steamed semi-micro Kjeldahl flask (60 ml.) using not more than 30 ml. total washings. Attach this flask to the distillation apparatus shown at the left of the figure, add 7 ml. of 48% NaOH through the stopcock and steam distill, slowly at first, into the receiver containing 10 ml. of 4% boric acid and indicator, until 25 ml. have distilled. Lower the receiver and distill about 5 ml. more. Cool flask, if necessary, and titrate with 0.010 to 0.015 N HCl. The end point is determined by the most distinct color change observable, usually from neutral gray to pink. Run all blanks to the same end point color. The use of a micro buret has little advantage because it requires about 0.02 to 0.03 ml. to cause an observable change in color at the end point. For lard oil runs, run a blank lard oil sample through the entire procedure. For lactic acid water solutions, run a blank distillation only, containing 2 ml. of the same H_2SO_4 as used for the run. The indicator is a mixture of 25 ml. of 0.1% Brom Cresol Green in 90% alcohol with 5 ml. of 0.1% Methyl Red in 90% alcohol. Use 3-4 drops. Dilution will change indicator color so a standard procedure must be adopted.

Calculations:

Volatile N compound as acrylonitrile, parts per million (micrograms per ml.) =

$$\frac{(A-B) \times N \times 53{,}000}{30}$$

A = ml. HCl used for run
B = ml. HCl used for blank
N = normality of HCl

Report only to nearest whole number for low values.

B. Analysis for Hydrogen Cyanide

The method used is essentially that described by Gettler and Goldbaum, Anal, Chem., 19, 270 ('47). In this case the aeration tube is a 30 ml. test tube connected with an absorbing tube and finally to the flanged orifice for holding the test paper described in the above paper. The 10 mm. orifice was used for this work

Set up the apparatus as shown at the right in Figure I, putting about 0.5 ml. of 6N H_2SO_4 in the absorption tube. Grease should be used on all glass joints. Place 10 ml. of solvent from a freshly opened flask in the test tube. If it is a water solution, add about 1 ml. of 6 N H_2SO_4 and rapidly attach the test tube to the system. It is lard oil, simply attach to the system. A very small amount of trichloracetic acid may be added to the lard oil but it does not appear to be necessary and appreciable quantities cause darkening of the test paper. Turn on suction very gently, place a water bath under the test tube and heat to near boiling. At this point with a water solution in the tube, turn on full water aspirator suction for 5 minutes. With lard oil in the tube, continue a moderate flow of air for 5 minutes, then increase suction to full flow and allow it to run for 10 minutes. The pores of the test paper will clog and slow down the flow after 2-3 minutes in both cases. Toward the end of the time period heat the absorption tube and connecting tubes with a flame.

Remove the test paper from the flanged holder and immerse it in 1:4 HCl until it is completely wetted and for an additional minute. Wetting time is often 3-4 minutes. Wash for about 1 minute in distilled water and dry the paper by heating in air. Compare the intensity of color with standards made by the same process and kept between glass

microscope slides. Estimate the hydrogen cyanide only to the nearest microgram. The concentration in the solution is then, micrograms found divided by 10, expressed in parts per million volumes of solvent.

C. Analysis of Film for Extraction Loss.

1. Lard Oil Immersions.

Remove film from flask, wash with petroleum ether, place it between filter papers, roll into shape to fit a Soxhlet extractor and extract with petroleum ether for 48 to 72 hours. A satisfactory extractor to use is one with a capacity of about 200 ml. of liquid, emptying every 12 minutes. A smaller extractor might cut the time required to reach constant weight.

2. Lactic Acid Solution Immersions:

Remove the film, wash with distilled water and dry in 105° C oven for about 1 hour, or to constant weight. Calculate loss of weight based on original film weight.

Checking of Analytical Procedures

Prior to the establishment of the present method, analysis for acrylonitrile was attempted by polarographic examination of vapors swept from the solution into methanol. The method was not sufficiently sensitive and vapors from the lard oil caused interference. It was then established that if acrylonitrile is dissolved in concentrated H_2SO_4 or is caught in it by means of absorption tubes that the nitrogen can be quantitatively determined by distillation as ammonia from an alkaline solution. No catalyst or heating is necessary, but the acid must be concentrated and there is some indication that the time in contact with acid may be a factor. One hour is sufficient.

Nesslerization of the distilled ammonia would appear to be a more sensitive test. However, vapors carried over from the lard oil are also carried over in the distillation and result in heavy turbidity in the Nessler's reagent.

It was necessary then, to adopt the volumetric method as described. This method proved to be accurate within 10% of the amount of acrylonitrile present with water solutions. With lard oil solutions, made by adding small quantities of a

standard lard oil solution of acrylonitrile to samples of lard oil, the recovery by the method described is within 10% for over 100 micrograms of acrylonitrile and within 20% for smaller quantities. The limit of estimation, however, is about 30 micrograms of acrylonitrile, which gives a titration of only about 0.04 ml. greater than the blank. The reproducibility of the blank is about 0.01 ml.

It must be kept in mind that the method will also determine amines or other volatile nitrogen compounds which will yield ammonia during the distillation process.

The hydrogen cyanide (HCN) method was calibrated with water solutions using the method as described in the literature. The ferrous-ferric caustic test papers were used as described and standard colors which were reproducible to about 0.5 micrograms were obtained for comparison. For HCN in lard oil, standard oil solutions were prepared by successive dilutions of a sodium cyanide solution with alcohol containing trichloracetic acid and finally with lard oil. Only about 0.1 ml. of alcohol was present in the final test solution. It was found that from 2 to 5 micrograms of HCN gave test papers essentially as intense as the corresponding water solution runs. However, because of a slight brown coloration always obtained from the lard oil, 1 microgram could not be detected. 1 microgram is only just visible from a water solution. Therefore, a negative test has been considered to be less than 2 micrograms of HCN (0.2 p.p.m.) in lard oil, It is probable that the use of the smaller orifice described by Gettler and Goldbaum would increase the sensitivity of this test if the need arises.

Composition of Films:

Each of the films contains as its base a mixture of a vinyl resin (either Geon 202 or vinylite VYDR) and Perbunan 35NS90 rubber. In addition to these two basic ingredients they contain minor quantities of, (a total of about 5%) mono glyceryl oleate edible A, acrowax, and santocell C. The difference in the two films, aside from minor variations in relative amounts of the basic ingredients, is that 012212 contains Geon 202 resin while 012220G contains vinylite VYDR resin.

Results:

The results of the investigation are summarized in Table I:

TABLE I

012220G Film

Immersion 30 days at 100° F., plus about 15 days at room temperature.

Sample No.	Pet. ether extract%	Pet. ether alone, %	HCN p.p.m.	Acrylonitrile p.p.m.
1	2.94	2.97	<0.2	<1
2	3.10	3.03	<0.2	<1
3	2.98	3.06	<0.2	<1
4	Lost		<0.2	<1
5	2.90		<0.2	<1
6	3.08		<0.2	<1
Avg.	3.00	3.02	<0.2	<1

012212 Film

Immersion 30 days at 100° F., plus about 30 days at room temperature.

1	4.25	4.18	<0.2	<1
2	4.20	4.26	<0.2	<1
3	4.30		<0.2	1
4	4.30		<0.2	1
5	4.20		<0.2	<1
6	4.20		<0.2	<1
Avg.	4.25	4.22	<0.2	<1.0

012220G Film

Immersion in dilute lactic acid solution (ph 4.0) 30 days at 100° F., plus 20 days at room temperature.

Sample No.	Lactic acid soluble % of film	HCN, p.p.m. in solution	Acrylonitrile, p.p.m. in solution
1	0.54	0.1	1
2	0.56	0.1	1
3	0.54	0.2	1
4	0.70	0.1	1
5	0.64	0.1	1
6	0.64	0.1	1
Avg.	0.60	0.1	1

012212 Film

30 days immersion in dilute lactic acid (pH 4.0), plus about 30 days at room temperature

1	0.55	0.2	3
2	Lost	0.3	3
3	0.60	0.2	2
4	0.50	0.3	3
5	0.85	0.2	2
6	0.65	0.3	2
Avg.	0.63	0.25	2.5

Immersions were for 30 days at 100° F., plus varying periods at room temperature as indicated in the above table. Approximately one gram of the film was used in each of the tests. From an intimate knowledge of the film composition the theoretical solubility of various ingredients of the film in lard oil, petroleum ether, and water can be determined. These values are given in the first 2 columns of tables 2 and 3. By comparing these values with the results found in Table 1 the conclusion expressed in the last 2 columns of tables 2 and 3 can be drawn.

Table II

Lard Oil Solubility of Polymer

Non-polymer portion sol. in lard oil plus pet. ether, % of film		Film	Actual Sol., % of film	Pet. Ether Sol., alone % of film	Possible polymer, dissolved, % of film	
Minimum	Probable				Maximum	Probable
2.45	2.75-3.0	012220G	3.0	3.0	0.55	0
3.0	3.5 -4.0	012212	4.25	4.20	1.25	0.0-0.5

Table III

Lactic Acid Solution Solubility of Polymer

Non-polymer water soluble, % of film		Film	Actual loss of Weight % of film	Possible polymer dissolved,% of film.	
Minimum	Probable			Maximum	Probable
0+	0.3-0.6	012220G	0.60	0.60	0-0.3
0-1.3	0.5+	012212	0.63	0.63	0.1

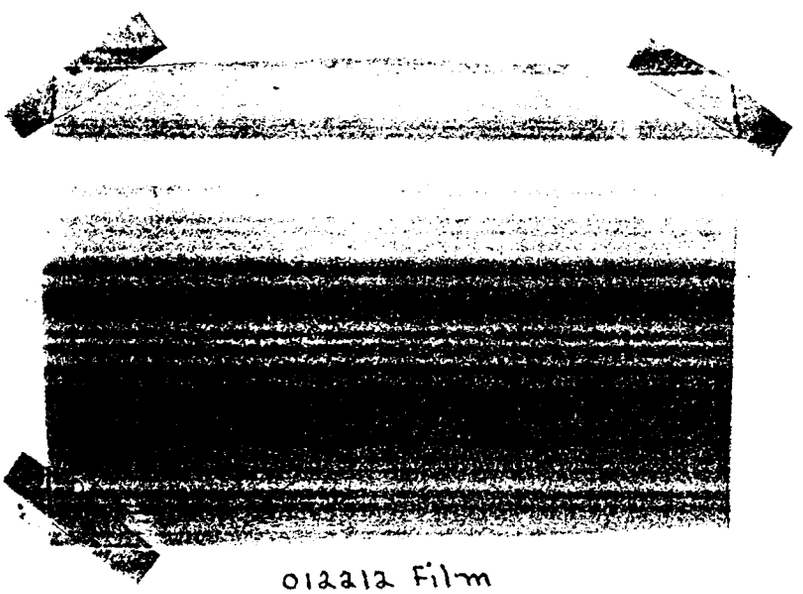
The qualitative test for appreciable quantities of polymer soluble in lard oil used by Battelle Memorial Institute in a quantitative manner was tried on these samples of lard oil after the immersion period. Comparison of the blank lard oil with the lard oil from runs in 5 inch columns of liquid gave no indication of turbidity. Dilution 1:1 and 1:3 with petroleum ether followed by thorough mixing caused a slight turbidity but it was fully as great, to the eye, in the blank solution as in the ones in which film had been immersed. These tests indicate only, that there was no appreciable quantity of polymer suspended in the lard oil. The actual solubility under such conditions would be a function of the particular polymer. However, rather small quantities of polymer will normally precipitate or cause turbidity when the oil is siluted with hydrocarbons.

Summary:

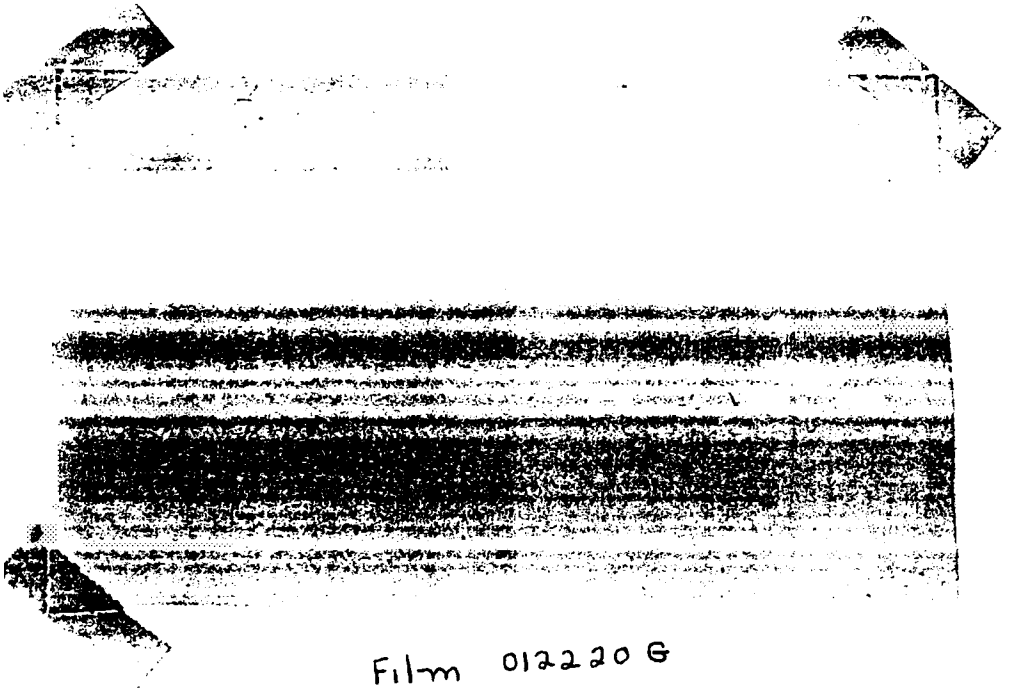
These data can be put in another form to demonstrate the effect of this solubility on any food product of a nature such as lard oil or aqueous lactic acid solution. If it is assumed that the % of soluble film polymer can be projected on the basis of the wrapping for a pound of oleomargarine or meat, then the films which weigh about 3 grams per pound of food would have a maximum polymer solubility of 17 parts per million (01220G Film) and 38 parts per million (012212 Film). They would probably have a maximum solubility of about 18 parts per million each, if the package is in contact with only lean meat, the liquid content of which would approximate dilute lactic acid solution.

The figures on hydrogen cyanide and acrylonitrile indicate that under the worst possible conditions there could be no more than 0.25 parts per million of hydrogen cyanide or 1 part per million of acrylonitrile present per pound of food.

February 24, 1949.



012212 Film



Film 012220 G