cc J Best 2/5/71

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February 5, 1971

TO: All Members of the SPI Food, Drug and Cosmetic Packaging Materials Committee.

Gentlemen:

Having just received a letter and the FDA suggested procedure for extraction testing on pigmented plastics mentioned at our January 13 meeting, I am writing to supply this information to you. At the same time, however, I thought I would take the opportunity to inform the Committee on an interim basis about two other subjects of interest so I hope you will not mind receiving something of an "omnibus" report.

Firstly, we are enclosing herewith a copy of a February 2, 1971 letter from Al Holtz of the Food and Drug Administration, along with a copy of the extraction methodology mentioned therein. We would appreciate it if all of you with an interest in the pigments situation would review the methodology and send us any comments you care to make at your earliest convenience. Since the comments are apt to be technical in nature, it would be helpful if you could send copies of anything you have to say to Bill Westveer, the Chairman of our Technical Information Committee and to George Ingle who is acting as Chairman pro tem of the Pigments Task Group.

Depending on the nature of the comments received, we may well decide to meet with the Food and Drug Administration staff on this matter sometime in March, probably on March 25, so that the

entire situation can be discussed with Mr. Holtz and his associates. Thus, we do hope you can review the enclosed and give us your thoughts by no later than March 10, 1971.

Regarding the minutes of the January 13 meeting, we had hoped to have them completed before now but we have been delayed while we were awaiting one of the liaison reports expected. We are now proceeding with the final typing so the minutes should be in your hands within the next two weeks, the additional time being required to accomplish reproduction and distribution by the SPI office.

Finally, and as what I hope will be nothing more than an interim report, we did have a meeting with members of the Food and Drug Administration staff on the so-called "Ramsey proposal" on February 3, as scheduled. You will recall that this meeting was set up at the suggestion of Tom Brown of the Food and Drug Administration during our question and answer session on January 13. At that time, Mr. Brown indicated that he thought we could move the Ramsey proposal ahead if we could delegate two or three people to work with the staff promptly. Thereafter, we cleared the Frawley-Wulfsberg-Heckman delegation with the Inter-Industry Committee representing all of the major packaging association interests and notified the Food and Drug Administration that we were prepared to get together on February 3.

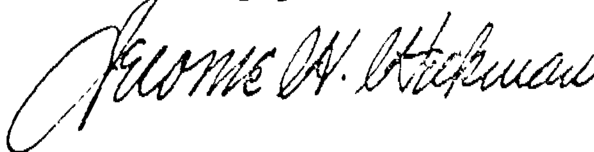
At the session with FDA, those in attendance from the Administration were Les Ramsey, Lou Buckley, Al Holtz, and Joe McLaughlin. To our great surprise--I might even more properly say shock--although we had lengthy discussions during which it was generally agreed that the Ramsey proposal remains, in Mr. Ramsey's opinion, "scientifically sound" we were told that Mr. Ramsey

did not believe it could be published as a final amendatory regulation to Section 121.2500, nor even as a proposal at this time, because "it would not be administratively [or to use my word, politically] advisable under current general conditions." As we read it, what Mr. Ramsey is saying is that he does not believe the Food and Drug Administration should have the courage to proceed with a helpful rules revision despite its scientific soundness at a time when FDA is under such fire because of situations like those involving the GRAS list review.

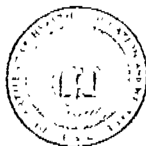
To put it mildly we were very disappointed with this advice. Furthermore, I am still unable to believe that this result is what Tom Brown had in mind when he suggested at our meeting that we work together to further our mutual interests. For this reason, and especially since Mr. Brown was not in attendance on February 3, I am now planning to be in touch with him on this very important subject once again, hopefully when he returns to Washington on Monday or Tuesday of next week. All I can add at the moment is that I hope this effort to move past Mr. Ramsey will be fruitful. In any case, this interim report should serve to bring all of you completely up to date for the time being.

If anyone receiving a copy of this letter has a question about any of the subjects discussed before we are in touch once more, please do not hesitate to call or write.

Cordially yours,



Enclosure



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
FOOD AND DRUG ADMINISTRATION
WASHINGTON, D.C. 20204

February 2, 1971

Mr. Jerome H. Heckman
1712 N Street, N.W.
Washington, D.C. 20036

Dear Jerry:

Attached is a copy of our suggested procedure for extraction testing on pigmented plastics which you requested (1/15/71). This is the method which was mentioned at the recent SPI meeting and is essentially the one which Eastman evaluated for their petition. This version includes some modifications introduced to answer some of Eastman's questions and which they considered desirable.

Our interest in submitting the above through you to several other interested parties is to derive the benefit of varied trials and/or viewpoints towards providing a standard acceptable procedure.

Our August 1966 Guidelines should also be consulted for any pertinent information relating to this special extraction subject.

If any questions arise concerning this tentative method we will be glad to discuss them.

Thank you for your help and cooperation.

Sincerely yours,

Attachment

A. Holtz, Chemist
Food Additives Petition
Evaluation Branch
Division of Food Chemistry
and Technology

COLOR EXTRACTION TEST FOR POLYMERIC MATERIALS

A. Extraction of rigid or semi-rigid food-contact containers.

(i) Equipment

(1) 800 ml beakers with watch glass covers
(2) Tared 250 ml beaker
(3) 2-1/2 inch square stainless steel screening sufficient for the replicates needed.
(4) Paper clip or other clipping device to hold screen and sample sandwich together.
(5) Suspending wire to hold sample sandwich in beaker.
(6) Tongs
(7) Hot air oven
(8) Thermostatically controlled waterbath to ± 1.0° F., variable from 80° F. to 135° F., capable of holding 800 ml beakers.
(9) Hood and hot plate facilities
(10) Analytical balance of suitable sensitivity (0.1 mg) and capable of handling the 250 ml beaker.
(11) Desiccator

(ii) Reagents.

(1) Freshly deionized distilled water
(2) Freshly redistilled, reagent grade n-heptane b. pt. 208° F.
(3) 95 percent (by volume) ethyl alcohol, diluted with deionized distilled water to 8 percent and 50 percent by volume.
(4) Freshly distilled acetic acid diluted to 3 percent (by volume) with deionized distilled water.

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(iii) Test materials

Select a sufficient number of rigid or semirigid containers so as to be able accurately to cut eight 2-1/2 inch square samples or other desirable samples from the formed products for the test material.

(iv) Procedure

(a) Total non-volatile extractives

(1) Determine the appropriate solvents and extractability conditions for the intended uses as described in section 121.2526(d) Tables 1 and 2. For the normal packaging of thermoplastics we consider 120-30° F a self-limiting temperature.

(2)(a) Using the tongs, carefully prepare two sandwiches consisting of screen, sample, screen, sample, screen, sample, screen, sample, screen. Clip each sandwich together by means of the clipping device.

(b) Introduce 100 ml of the appropriate food simulating solvent in an 600 ml beaker using each of the four food simulating solvents named above (water, 3% acetic acid, alcohol (8% or 50%) and n-heptane, cover with a watch glass, and place in the constant temperature bath and condition at the desired temperature.

(c) After conditioning, carefully introduce the sample sandwich into the appropriate extracting liquid.

(d) Extract using the appropriate solvents and time-temperature conditions.

(3) If the procedure under (2) is not readily applicable then use the following immersion method.

Extract the samples as necessary (by film or plaque immersion etc.) with proper aliquot sampling at optimum intervals until equilibrium (i.e. no change in extraction level) as gauged by at least 3 periodic tests at the same temperature covering at least 72 hours for aqueous and 6 hours for heptane.

(4) At the conclusion of the extraction period, carefully suspend the sandwiches by the wire to drain into the beaker.

(5) After draining, pour the food simulating solvent solution into the tared beaker. Rinse the 800 ml beaker three times with the required solvent, using a total of not more than 50 ml.

(6) Evaporate the liquid to a few milliliters on a low temperature hot plate, transfer to an oven at 221° F. and evaporate to dryness. Allow to cool in a desiccator to room temperature and weigh the residue to the nearest 0.1 mgm. Calculate the total extractives in milligrams per square inch of container surface.

(7) When running the acidic and alcoholic extractions, the sampling and analyses on these need not be started until the point where the water extraction reaches equilibrium. If these extractives are of the same type and equal or less than the water value level then we can consider these at equilibrium. If however, their ranges are 10-15% greater, then the acidic and/or alcoholic extractions should be continued to equilibrium.

(b) Amount of colorant extracted.

Dissolve the weighed residue in deionized water or required concentration of reagent grade nitric acid, if necessary, neutralizing the acid with reagent grade sodium hydroxide solution after the residue is dissolved.

Proceed as described for flexible surfaces.

B. Extraction of flexible polymeric food-contact surfaces.

(i) Equipment

(1) Extraction test cells described in Methods of Analysis, AOAC, sec. 7,035, 7,037.

(2) Oven rack for extraction test cells

(3) Hot air oven

(4) Graduated cylinder

(5) Fritted glass filter

(6) Platinum evaporating dish

(7) Steam bath

(8) Desiccator

(9) Analytical balance of appropriate sensitivity (0.1 mg)

(ii) Reagents

(1) Freshly deionized distilled water

(2) Freshly redistilled, reagent grade n-heptane, b.pt. 208° F.

(3) 95 percent (by volume) ethyl alcohol, diluted with deionized distilled water to 8 percent and 50 percent by volume.

(4) Freshly distilled acetic acid diluted to 3 percent (by volume) with deionized distilled water.

(iii) Test materials

Select samples of flexible food-contact films and protect from exposure to liquids or contact with other materials and from wrinkling or abrasion. Cut in rectangles equal to or exceeding the dimensions of the extraction cell with 1 dimension at least equal to or greater than the 8" width of the cell, and sufficient for 2 rectangles to each cell and for 2 cells per determination.

(iv) Procedure

(a)(1) Total non-volatile extractives:

(1) Determine the appropriate solvents and extractability conditions for the intended use(s) as described in section 121.2526(d) Tables 1 and 2.

For normal packaging of thermoplastics we consider 120-130° F a self-limiting temperature

(2)a. Follow the test procedures set forth in Official Methods of Analysis of the AOAC 7.037, 7.038, and 7.039, using the appropriate solvents and temperature conditions.

(b) If the procedure under (2)(a) is not readily applicable then use the following immersion method.

Extract the samples as necessary (by film or plaque immersion etc.) with proper aliquot sampling at optimum intervals until equilibrium (i.e. no change in extraction level) as gauged by at least 3 periodic tests at the same temperature covering at least 72 hours for aqueous and 6 hours for heptane.

(3) When running the acidic and alcoholic extractions, the sampling and analyses on these need not be started until the point where the water extraction reaches equilibrium. If these extractives are of the same type and equal or less than the water value level then we can consider these at equilibrium. If however, their ranges are 10-15% greater, then the acidic and/or alcoholic extractions should be continued to equilibrium.

(4)(a) Calculate the total extractives in milligrams per square inch of container surface.

(b) In calculating migrations of milligrams per square inch, the area of the exposure used is only that of one side if the film used is less than 5 mils.

(5) Amount of colorant extracted.

Dissolve the weighed residue in deionized water or required volume concentration of reagent grade nitric acid, if necessary, neutralizing the acid with reagent grade sodium hydroxide solution after the residue is dissolved.

If the colorant is a metallic compound carefully evaporate the solution to about three drops and examine for the metal by means of suitable quantitative techniques with a maximum detection limit of about 0.05 micrograms of the metal. Calculate amount extracted per square inch of contact surface.

If the colorant is an organic substance, the residue solution should be made up to a standard volume with deionized distilled water or other appropriate solvent and the concentration of colorant determined chromatographically or spectrophotometrically by comparing the results from an uncolored film under test. The sensitivity of the technique use should be shown.

Do you compare residue chromat. or spectro?

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The results of the total extractive determination are to be used as a check on the equilibrium conditions and where appropriate to determine the compliance of the base film with the existing regulations.

Our suggested general analytical procedures are not necessarily binding. Any satisfactory validated method and sensitivity will be accepted.

cc: BF-100, BF-112, BF-301, BF-117, BF-148, BF-350(Mr. Spiher).

AHoltz:mcs 9/23/70
D/Init: MProchazka 9/23/70

If pigment a metal salt method OK but
if pigment is an organic material feel that comparison
with unpigmented sheet would be quite [illegible]

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before using, at rate of 15 ml

zide soln for washing.— ...ot <2.5% NH_3 by wt.

ARATION OF SOLUTION

e with little $Mg(NO_3)_2$ soln, lissolve in HCl (1+2.5), and In aliquot of soln det. P_2O_5 as

TERMINATION

prepd soln into 250 ml beaker; ght excess and barely dissolve w drops HNO_3, stirring vigor- $_2SO_4$ has been used as solvent, . NH_4NO_3 or soln contg that oln add 70 ml molybdate soln, 100 mg P_2O_5 present. Digest 1 st for complete pptn of P_2O_5 by date soln to clear supernatant. ith cold H_2O or preferably with . Dissolve ppt on filter with nd hot H_2O, and wash into >100 ml. Neutralize with HCl, r or *bromothymol blue* as indi- from buret add slowly (ca 1 . vigorously, 15 ml of the mag- g P_2O_5 present. After 15 min. H and let stand until super- ially 2 hr); filter, wash ppt with til washings are practically Cl- heat, and ignite to constant nace at 950–1000°; cool w... as $Mg_2P_2O_7$. Report as

ative Test—Official, Final Action

) to 1-2 g sample in 150 ml t acid with HNO_3, filter, take e and NH_4 molybdate soln, m at 40–50°. Yellow ppt indi- phosphate.

(10)—**Official, Final Action**

1.5 hr with mixt. of 300 ml H_2O lter, wash filter thoroly with hot d filtrate and washings, and dil.). Det. sulfate in 100 ml aliquot

nia—Official, Final Action

in distn flask add 300–400 ml of NaOH soln (1+1), connect nd distill into measured vol. std acid in distillate with std alkali,

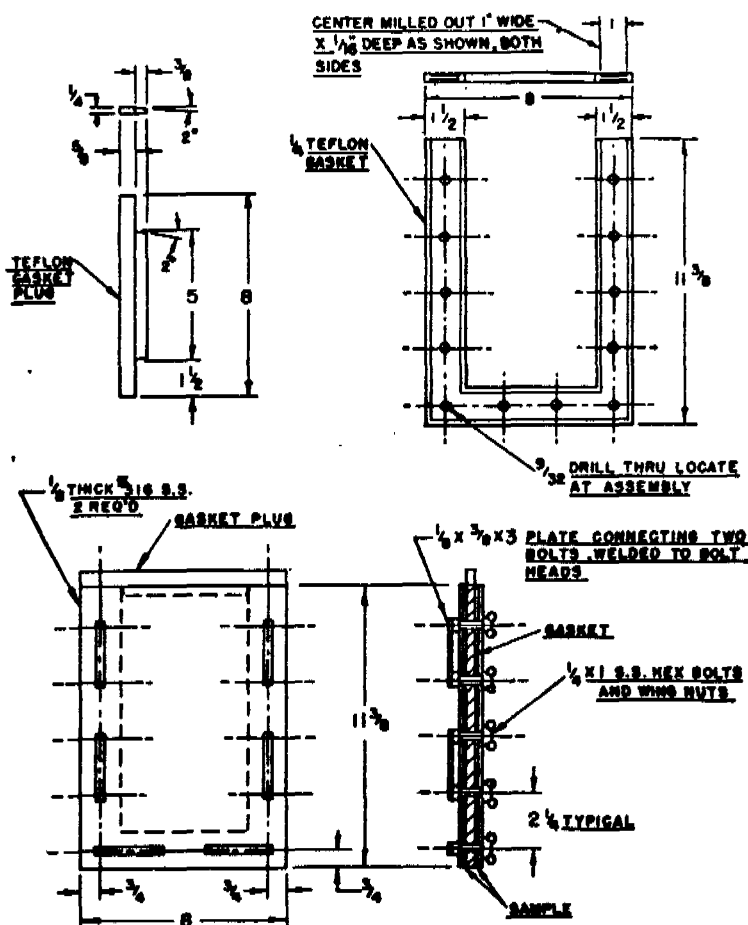

FIG. 7:2.—TEST CELL

7.031 Arsenic—Official, Final Action

Place 5 g sample directly in generator, 24.007(a); add 10 ml H_2O, little at time to prevent foaming over, and then 15 ml As-free HCl, adding it dropwise until foaming ceases. Heat on steam bath until drop of mixt., when dild and treated with I soln, does not show blue. Then dil. to ca 30 ml with H_2O and continue as in 24.010, beginning "add 5 ml of the KI reagent . . ." Prep. blank and stds for comparison, using As-free HCl of same concn as that used in detn.

7.032 Fluorine—Official, Final Action— *See 24.029–24.035*

7.033 Lead—Official, Final Action— *See 24.041–24.053*

FOOD ADDITIVES

Exposing Flexible Barrier Materials for Extraction

ASTM-AOAC Method (11)—Official, First Action

7.034 PRINCIPLES

Method provides std liquid extn method for flexible barrier materials, singly, coated, or combined, including extns thru flexible barrier materials of surface coating ingredients by food-simulating solvents. Specimens of flexible barrier materials are exposed to extg liquids in test cell and amount of nonvolatile extractives remaining after exposure is measured.

7.035 APPARATUS

(a) *Test cell.*—See Fig. 7:2. Consists of two 8×11½×¼" No. 316 stainless steel plates, de-

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greased; one ¼×1½" U-shaped virgin TFE-fluorocarbon (Teflon) gasket, grooved on both sides as shown; twelve ¼×1" stainless steel bolts with wing nuts; one ¾×1×8" TFE-fluorocarbon gasket plug tapered to provide tight fit. (Available from Scientific Products, Inc., Div. of American Hospital Supply, Evanston, Ill., No. 6200.) To prep. app. for use, wash plates and gaskets in aq. detergent soln. Rinse with H_2O and dry at 100°. Wash with *n*-heptane and redistd acetone. Immerse new gaskets in *n*-heptane overnight. Rinse gaskets with fresh *n*-heptane and dry at 100°.

(b) *Oven rack*.—See Fig. 7:3. To hold extn test cells.

(c) *Hot air oven*.—With safety provisions for flammable solvents. Vac. oven or autoclave is suitable.

7.036 REAGENTS

Use solvents (usually H_2O, dil. alcohol, and *n*-heptane) specified in regulations (Code of Federal Regulations, Title 21, Sec. 121.2514(d)(2); 121.2526(d)). Solvent for blanks and detn should be from same container.

7.037 PREPARATION OF CELLS

Select samples of flexible barrier material and protect from exposure to liquids or contamination by migration from contact with other materials, and from wrinkling or abrasion. Samples shall equal or exceed dimensions of cell where possible, and shall in all cases have 1 dimension equal to or greater than width (8") of cell.

Place 1 stainless steel plate of cell on flat surface with bolts protruding up thru holes in plate. Place prepunched specimen (side to contact liquid up) on plate with 1 edge aligned with bottom of plate, 2 edges aligned with sides of plate, and bolts passing thru prepunched holes. Place gasket on specimen with outer edges of gasket aligned with cell bottom and sides. If desired, place second prepunched specimen (side to contact liquid down) on top of gasket. If only 1 sheet is used for test, place inert barrier sheet such as Teflon or electrolytically cleaned tinfoil in place of second sheet. Place second stainless steel plate on top of assembly. Place wing nuts on bolts and tighten.

Preheat assembly (including TFE-fluorocarbon gasket plug) to test temp. and retighten nuts so that assembly is liquid-tight.

7.038 DETERMINATION

Place measured vol., *A*, of extg liquid, preheated to test temp., into assembly. Use vol. of liquid such that top of liquid is 0.5" below top of specimen. In no case should vol. of extg liquid be >200 ml. Insert gasket plug in top of cell. Expose cell in rack in oven to conditions of time and temp. specified by regulations. If vac. oven is used, operate it at atmospheric pressure. Align cells in rack in oven parallel with air flow.

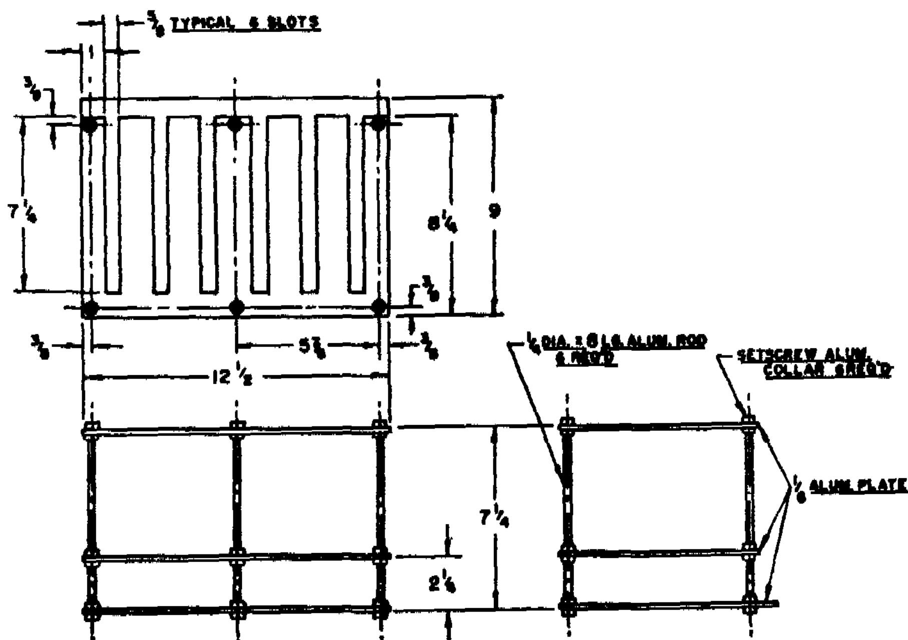


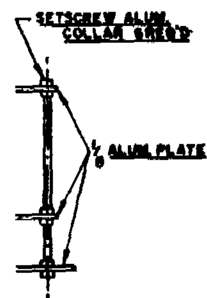
FIG. 7:3.—OVEN RACK

ASI-PR 0001184

ive 1 dimension equal to or
of cell.
of cell on flat surface
holes in plate. Place
(side to contact liquid up)
igned with bottom of plate,
les of plate, and bolts pass-
oles. Place gasket on speci-
of gasket aligned with cell
desired, place second pre-
e to contact liquid down)
ly 1 sheet is used for test,
t such as Teflon or electro-
l in place of second sheet.
teel plate on top of assem-
bolts and tighten.
cluding TFE-fluorocarbon
mp. and retighten nuts so
tight.

ERMINATION

, *A*, of extg liquid, pre-
nto assembly. Use vol. of
liquid is 0.5" below top of
ould vol. of extg liquid be
plug in top of cell. Expose
conditions of time and
ulations. If vac. oven is
nospheric pressure. Align
allel with air flow.



After exposure, remove cell from rack, remove gasket plug, and immediately pour out extg liquid into graduate. (If solids flake from specimen and it is desired to det. only sol. materials, filter thru fritted glass filter from cell into graduate.) If vol. of extg liquid is <90% of original vol., investigate cause.

Det. total nonvolatile extractives by evapg total vol. extg liquid to apparent dryness in weighed Pt evapg dish on steam bath. Dry in oven 30 min. at 100°. Cool 30 min. in desiccator and weigh.

Perform at least 2 blank detns with 200 ml extg liquid each and glassware that will be used in detn. Preclean glassware with chromic acid soln followed by H_2O rinse. Place equal vol. extg liquid into each of blank-receiving containers. If filter is used on extg liquid from exposed samples, include contact of solvent of blank with filter. Wt blank must be <2.0 mg/200 ml and <30% of wt extractives.

7.039 CALCULATION

With 2 sheets in cell, ratio of exposure area to vol. extg liquid used to fill cell is 2 ml/sq. in. Calc. mg extractives/sq. in. exposed sample = (mg extractives − mg blank)/sq. in. exposed sample.

Acetone Peroxides (*12*)—Official, Final Action

7.040 *In Baking Premixes*

Weigh accurately ca 8 g sample into flat-bottom centrifuge bottle, pipet 100 ml H_2O onto sample, and stir 10 min. after making sure no lumps remain. Centrifuge at ca 1500 rpm ca 10 min. Pipet 25 ml supernatant into erlenmeyer, add 25 ml H_2SO_4 (1+4), and let stand at least 3 min., swirling occasionally. Titr. to light pink that lasts >20 sec. with std 0.1*N* $KMnO_4$ soln, 42.023–42.024.

Total peroxides in g H_2O_2 equiv./100 g premix = ml $KMnO_4$ × normality × 0.0170 × 100/0.25 × g sample.

7.041 *In Milling Premixes*

Weigh accurately ca 200 mg sample into erlenmeyer, add 50 ml H_2SO_4 (1+9), let stand >3 min., stirring occasionally, and titr. with std 0.1*N* $KMnO_4$, 42.023–42.024, to light pink that persists >20 sec.

Total peroxides in g H_2O_2 equiv./100 g premix = ml $KMnO_4$ × normality × 0.0170 × 100/g sample.

Qualitative Test

(Acetone peroxides are extremely explosive. Do not ext. more org. peroxides from adsorbents than necessary for test.)

7.042 APPARATUS

(a) *Recording infrared spectrophotometer.*—Suitable for work from 2 to 16 μ.

(b) *Rock salt plate.*—Or other support stable to acetone and acetone peroxides and transparent in 2–16 μ region.

7.043 TEST

Weigh sample contg ca 10 mg H_2O_2 equiv. of acetone peroxides into g-s. flask. Add ca 1 g anhyd. Na_2SO_4 and 10 ml acetone for every g adsorbate. Shake 3 min., filter (Whatman No. 12 paper has been found satisfactory) or centrifuge (for baking premix), and carefully evap. clear soln to ca 1 ml under vac. at room temp.

Under warm light and gentle current of dry warm air, add concd acetone ext. dropwise to rock salt plate. When film of viscous liquid is visible on plate, place it in infrared light path and, without recording, check transmittance of peak at ca 12.1 μ. If necessary, add enough addnl portions of ext. to give 20–25% transmittance. Set spectrophotometer at acetone peak at ca 9.2 μ. Let radiation pass thru sample on plate until raised pen reaches max. transmittance (acetone has evapd). Then record spectrum of film on salt plate from 2 to 16 μ.

Compare curve to one obtained from reference acetone peroxides treated in same manner.

Nitrites (*13*)—Official, First Action

(Applicable to dry cure mix or curing pickle)

7.044 APPARATUS

Bend piece of glass tubing 250 mm long, 6 mm o.d., to form right angle ca 60–70 mm from one end. Connect short end with rubber tube to outlet of pressure regulator on CO_2 tank.

7.045 PREPARATION OF SAMPLE

(a) *Dry cure mix.*—Weigh 50.0 g sample and dissolve in 1 L H_2O. Transfer 25 ml aliquot to 250 ml erlenmeyer.

(b) *Pickle soln.*—Filter thru dry paper. Weigh 50.0 g filtrate into 250 ml erlenmeyer.

7.046 DETERMINATION

To soln in flask, add 20 ml colorless 15% KI soln and ca 2 ml starch soln, 17.001(g). Insert long end of gas inlet tube and adjust flow of CO_2 to ca 5 bubbles/sec. Continue flow of CO_2 thruout detn.

After ca 5 min., add 20 ml H_2SO_4 (1+7) from buret, and mix thoroly. Titr. with stdzd 0.0725*N* $Na_2S_2O_3$ to first complete disappearance of starch-I color. 1 ml 0.0725*N* $Na_2S_2O_3$ = 0.0050 g $NaNO_2$.

SELECTED REFERENCES

(*1*) J. Assoc. Offic. Agr. Chemists 6, 453(1923).
(*2*) Ibid. 10, 36(1927).
(*3*) Ibid. 31, 278(1948); 32, 83, 269(1949); 33, 77(1950).

ASI-PR 0001185