TESTING OF DIPHENYL AND AROCLORS

DSW 331903

SOFTENING POINT OF SOLID AROCLORS
Ball and Ring Method.

This method is a modification of the A.S.T.M. standard method of test for softening point of bituminous materials, serial designation: D 36-26. The method differs from the standard method in that the rings are larger than specified. A two ring support is also used in order that two tests may be made simultaneously.

APPARATUS

The apparatus consists of the following: (a) Two brass rings, 3/4" inside diameter and 1/2" deep; thickness of wall 3/32". (b) Two steel balls, 3/8" diameter weighing 3.45 to 3.55 grams each. (c) A 800 cc Griffin low form beaker. (d) A ring support for the two rings having a brass plate exactly one inch below the plate supporting the ring. (e) A 300°C A.S.T.M. low distillation thermometer graduated to 1°C.

PREPARATION OF THE SAMPLE

The sample shall be melted and stirred thoroughly, avoiding overheating or incorporating air bubbles in the mass and then poured into the ring so as to leave a slight excess on cooling. Since the Aroclors shrink considerably on cooling, the ring should be well filled, nearly to overflowing. A little of the excess should be drawn over the top of the ring at several points so as to prevent the cooled Aroclor from dropping out of the ring. In the same way, the second ring is filled with a standard Aroclor of known softening point. The standard Aroclor should have a softening within at least 10 to 15° of the Aroclor being tested.

The rings while being filled should rest on a clean can lid or on a brass plate which has been amalgamated to prevent the Aroclor from adhering to it. The Aroclor in the rings should be fully cooled and hardened before proceeding with the test.

PROCEDURE

Add cool c.p. glycerin (not above room temperature) to the beaker until the surface of the glycerin is 2" above the plate holding the rings when the ring support is suspended in the beaker. Place the rings containing the Aroclor to be tested and

73.5
73.0°

the standard Arocolor on the ring support. Place a ball on the center of the upper surface of the Arocolor in each ring. Suspend the thermometer so that the bottom of the bulb is level with the bottom of the rings and just midway between the two rings.

Place beaker and apparatus on a 6 inch round hot plate and heat at such a rate that the temperature is raised 5°C each minute.

The temperature recorded by the thermometer at the instant the Arocolor touches the bottom plate is reported as the softening point. The heating is continued until both Arocolors have dropped to the bottom plate. No corrections are made for emergent stem.

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NOTES

1. The standard Arocolor is run along with the sample under test in order to compensate for variations in rate of heating, dilution of glycerin, and thermometer variations.

2. The softening point of the standard sample is determined by making several determinations using fresh glycerin and carefully checking the rise in temperature of the glycerin so that it is as near as possible to 5°C per minute.

3. The glycerin may be used repeatedly for the tests after removal of the Arocolor.

4. Benzol is used for cleaning the rings and balls.

5. Water can be used instead of glycerin for softening points up to 90°C.

6. For softening points above 100°C, well boiled glycerin should be used. The usual glycerin is not satisfactory as at 125 to 130°C, it boils with loss of water while the temperature remains practically constant. It is well to have a supply of high-boiling glycerin on hand to be used only for softening points above 100°C.

7. Air bubbles on the rings and balls during the test should be avoided as far as possible.

8. The rate of rise of temperature of the glycerin shall be uniform for each minute after the first 3 minutes of heating and not averaged over the period of the test.

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DETERMINATION OF FREE CHLORIDES IN AROCLORS

Place approximately 50 grams of the Arocolor in a 250 ml Erlenmeyer flask. Add 100 ml distilled water and stopper loosely. Place flask in a water bath at 75°C and hold bath constant at 75°C for 30 minutes. Shake contents of flask vigorously every 10 minutes. At the end of the 30 minutes heating period remove the water from the flask and filter it to remove any turbidity. To the filtrate add 10 ml concentrated HNO_3 and 15 ml 0.1 N $AgNO_3$ solution. If any turbidity develoopes, determine the amount by colorimetric comparison, using standard solution of NaCl containing .001 gram cl/ml. If there are appreciable chlorides present a second water extraction should be made.

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DETERMINATION OF CHLORINE IN AROCLORS

Chlorine in Aroclors may be determined by fusion of the sample with sodium peroxide in a Brugess-Parr fusion cup, extracting the fusion with water, acidifying the water extract with nitric acid, and precipitating the chlorine by addition of an excess of silver nitrate. After filtration, the excess of silver nitrate is determined by titration against potassium thiocyanate, using ferric ammonium sulfate as indicator.

APPARATUS

The fusion cup used is the Burgess-Parr Sulfur Bomb No. 3 for flame ignition. A lead gasket is used. For ignition, the bomb is suspended through a 1-3/16" round hole in a 1/8" transite plate. This allows the fusion cup to extent through the plate for about 5/8". Ignition is effected by strongly heating the bottom of the fusion cup with the full flame of a Meker burner. The bottom of the cup should come to redness in not more than two minutes.

CHARGE FOR FUSION

The fusion mixture is made up of about 15 grams (one measure full) sodium peroxide powder, 0.3 gram of powdered cane sugar, and 1.0 gram of powdered potassium nitrate. The reagents must be free of chlorine or a blank must be run and the necessary corrections made. The fusion mixture must be well mixed and free of lumps.

Solid Aroclors: 0.3 gram of crushed sample (preferably 15 to 50 mesh) is added to 1/2 to 2/3 of the fusion mixture contained in the fusion cup. Mixing is accomplished by stirring with a narrow metal spatula, 1/8 to 1/4" wide. The remainder of the fusion mixture is then added to the fusion cup and the cover made tight by drawing down the screw cap.

Liquid Aroclors: 0.25 to 0.35 gram of sample is weighed by difference into a clean fusion cup. Rotate the fusion cup to distribute the liquid over the bottom. Add the fusion mixture which has been previously well mixed. Attach the cover tightly by drawing down the screw cap.

PROCEDURE

Place the fusion cup, which contains the prepared sample and fusion mixture, in the transite ignition plate and apply the full flame of the Meker burner to the bottom of the fusion cup for 4 minutes. CAUTION -- Do not stand too near the fusion during ignition.

Then remove the flame and after air cooling for 1/2 minute or more, place the cup in a pan containing about 3/4" depth of water. Let cool until boiling of water ceases, then remove screw cap. Thoroughly rinse the cup cover with water, collecting the rinsings in a clean 600 cc beaker.

Then place the fusion cup on its side in the beaker and cover with a watch glass. Add water slowly so that the fusion is decomposed without violent boiling. Remove the cup and rinse well. Heat the contents of the beaker to boiling and boil for about 5 minutes. Remove from heat and let cool for a few moments, then rinse off cover-glass and add pure 50% HNO_3, with stirring, until acid is present in excess to the extent of about 10 cc (About 50 cc of acid are required).

Cool the acidified solution in running water to room temperature, add exactly 50 cc of standard silver nitrate solution from a pipette and stir to effect coagulation of the silver chloride precipitate. Filter with suction through an asbestos pad on a 1-1/2" perforated porcelain plate and wash beaker and filter 5 times with small portions of cold water. Allow the filter to drain completely between washings. Transfer the filtrate back into the 600 cc beaker and rinse the flask twice, adding the rinsing to the beaker.

Add 5 cc of ferric iron indicator to the solution and titrate with standard KCNS solution until a distinct pink tint is just obtained.

CALCULATION OF CHLORINE CONTENT

Subtract the volume of KCNS required from the volume of KCNS required to titrate 50 cc of standard $AgNO_3$ solution. This will give the volume of KCNS equivalent to the chlorine in the sample. Multiply the volume so obtained by the chlorine value of each cc of KCNS and divide by the weight of sample taken.

For example: If 50 cc of silver nitrate solution is equivalent to 61.4 cc of KCNS solution and the value of 1 cc of KCNS solution is .003770 gram Cl; then if it is found that 0.3 gram of sample shows a KCNS titration of 10.4 cc, the percent of chlorine is:

$$\frac{(61.4 - 10.4) \times .003770 \times 100}{0.3} = 64.09\ \%\ Cl$$

In case the fusion mixture or other reagents contain chlorine, the amount must be determined and deducted from the chlorine found.

SOLUTIONS REQUIRED

Standard $AgNO_3$ solution: About 0.15 N; dissolve 22 grams of silver nitrate in each liter of water. Protect the solution from light. Fifty cc of this solution will precipitate by theory 0.23 gram of chlorine.

Standard KCNS solution: About 0.1 N; dissolve 10 grams of KCNS in 1 liter of water. 1 cc = about .0036 gram chlorine.

Ferric Iron Indicator. Use a saturated solution of ferric ammonium alum.

Pure Nitric Acid, 50%. Mix 500 cc of nitric acid, sp.gr. 1.40, with 300 cc of water and boil until the acid is colorless, thus insuring absence of lower oxides of nitrogen.

STANDARDIZATION OF SOLUTIONS

Weigh 0.3 and 0.15 gram portions of pure dry NaCl into separate 600 cc beakers. Add 250 cc of distilled water to each and 10 cc of pure 50% nitric acid. When solution is complete, add 50 cc of standard $AgNO_3$ solution from a pipette. Stir well and filter through an asbestos mat on a perforated porcelain plate, using suction. Wash filter and transfer the filtrate back to the beaker in the same manner as when working with a sample. Titrate the filtrates with standard KCNS solution, using ferric iron indicator.

The value of 50 cc of $AgNO_3$ solution in terms of KCNS solution is found by subtracting the cc of KCNS solution used in titrating the 0.3 gram of NaCl from twice the number of cc of KCNS solution used in titrating the 0.15 gram of NaCl.

This value is checked by titrating 50 cc of $AgNO_3$ solution added to 400 cc of water and 10 cc of pure 50% HNO_3 with KCNS solution. This titration should agree very closely (± 0.1 cc) with the value found from the titrations of NaCl. The titration must be made slowly to avoid drainage error.

Since pure NaCl contains 60.66% Cl by theory, the value of the KCNS interms of chlorine may be found by dividing the weight of chlorine in the NaCl taken by the cc of KCNS equivalent to the silver nitrate required.

Example: Two 0.3 gram portions of NaCl show KCNS titrations of 13.11 and 13.13 cc.

Two 0.15 gram portions of NaCl show KCNS titrations of 37.28 and 37.24 cc.

The KCNS equivalent to 50 cc of $AgNO_3$ is then (37.28 + 37.24) ÷ 13.12 or 61.4 cc.

By titration of 50 cc of $AgNO_3$ against KCNS solution, it is found that 61.36 cc are required. This agrees within .04 cc of the value obtained from the NaCl titrations.

The chlorine value of the KCNS is then: .6066 x .3 divided by 61.4 - 13.12 or .003770 grams Cl per cc of KCNS.

The chlorine value may also be calculated from the titration of 0.15 gram of NaCl. 0.6066 x .15 divided by 61.4 gives .003770 grams Cl per cc of KCNS.

NOTES

1 - The fusion materials have explosive properties if wrongly handled; consequently care must be taken to use safe proportions, to secure a good mixture free of large lumps, and to properly seat the cover of the fusion cup. The fusion mixture must be kept away from water or moist air, either of which may ignite the charge. The fusion mixture should not be ground to reduce lumps.

2 - On account of the high chlorine content of many of the Aroclors and the small amount of sample taken, great accuracy is required in weighing, transfer, and mixing of the sample. The pipette and burette for measuring the standard solutions must be very clean to avoid drainage errors.

4 - Solid Aroclors should preferably be about 15 to 50 mesh when weighed. If the sample is finely powdered there is difficulty in transfer of the material to the fusion dup due to jumping of the small particles when touched witha brush.

5 - Reasonable variations in the amount of excess HNO_3 present when titrating cause no difference in the titration.

6 - Boiling of the acidified solution before addition of silver nitrate causes slight loss of chlorine if the boiling is prolonged (15 to 30 minutes). Boiling at this point should be avoided.

7 - Fusions which show black carbon deposits on the cover and side of the fusion cup may or may not give the full chlorine content. If a carbon deposit is found, a second fusion should be made using a smaller sample or reducing the amount of sugar in the charge or both.

8 - Mixing the fusion charge by shaking after the screw cap has been drawn down may lead to incomplete fusions. The mixing of the sample with the fusion mixture should be done in such a way that the sample is fully covered with the mixture.

9 - The temperature at which the standard solutions are standardized should be noted. In case room temperatures vary from this temperature, appropriate volume corrections should be made.

10 - The fusion mixture materials should be essentially free of chlorine. The chlorine content may be determined by making a blank fusion, that is, without addition of sample, and titrating in the usual way. Five cc of $AgNO_3$ may be added instead of 50 cc. The KCNS titration is then compared with titrations of 5 cc portions of $AgNO_3$ solution in like volumes of solution and nitric acid.

11 - In case the solid samples are difficult to transfer without loss by brushing from the weighing pan of the balance, the sample should be weighed by difference from a small weighing bottle.

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DETERMINATION OF ACID NUMBER

ACID NUMBER OF DISTILLED AROCLORS

Dissolve 30 to 50 grams of sample in 50 cc of c.p. benzol contained in a 250 cc beaker. Add 50 cc of 95% ethyl alcohol, stir thoroughly and titrate with 0.01 N NaOH solution using 10 drops of 1% phenolphthalein solution as indicator. The end point is a faint pink color which is permanent for at least 2 minutes after vigorous stirring.

Determine the blank titration for the reagents by taking the same amounts of each (50 cc benzol and 50 cc alcohol) and titrating with the same 0.01 N NaOH using the same procedure and end point as in the determination.

Subtract the blank titration from the titration of the sample and calculate the acidity in milligrams of NaOH required per gram of sample. For .01 N sodium hydroxide solution the calculation is:

$$\text{MgM . NaOH/gm. sample} = \frac{\text{titration in cc x 0.4}}{\text{gms. of sample}}$$

Example: If 40 grams of sample give a titration of 2.7 cc of .01 N NaOH and the blank titration is 1.3 cc, then the acid number is: (2.7 - 1.3) x 0.4 divided by 40 = 0.014 Mgm. NaOH per gram of Aroclor.

ACID NUMBER OF CRUDE AROCLORS

Dissolve 20 to 50 grams of Aroclor (depending on the amount of acid present) in 50 cc of c.p. benzol contained in a 250 cc beaker. Add 50 cc of 95% ethyl alcohol and titrate with 0.5 N NaOH solution using 10 drops of 1% phenolphthalein solution as indicator. Calculate the acidity in milligrams of NaOH required per gram of sample. On account of the strong NaOH solution used for titration, the blank titrate of the reagents may be omitted.

$$\text{Mgm NaOH per gram sample} = \frac{\text{titration in cc x 20}}{\text{wt. of sample}}$$

Example: If the titration of 40 grams of sample is 1.2 cc, the acid number is found as follows: 1.2 x 20 divided by 40 = 0.60 Mgm NaOH per gram of Aroclor.

.60

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SODIUM HYDROXIDE 0.01 N

To prepare one liter of solution: Transfer 20 cc of 0.5 N NaOH measured by a pipette or burette to a liter volumetric flask. Fill to the mark with water and mix well. Unless the standard 0.5 N NaOH is considerably off from being exactly 0.5 N, no correction need be made for normality factor. To correct for the normality factor of a 0.5 N x 1.012 NaOH solution, multiply 0.4 by 1.012 (= .4048) to obtain the NaOH value of the .01 N solution.

NOTES

1. The term "acid number" is convenient in referring to the results of this test. The "acid number" is defined as the milligrams of NaOH required to titrate one gram of aroclor under the conditions described above.

2. The H. H. Robertson Company calculates the "acid number" on the basis of the milligrams of KOH instead of NaOH. Results in terms of NaOH when multiplied by 1.402 give results in terms of KOH. Conversely, results expressed in terms of KOH when multiplied by 0.713 give results in terms of NaOH.

3. The acid number multiplied by 1000 gives results in parts of NaOH required per million parts of Aroclor. For example, a distilled Aroclor requiring 0.014 Mgm. of NaOH per gram of Aroclor (acid number 0.014) may be also expressed as requiring 14 parts of NaOH per million parts of Aroclor.

4. If the acidity be calculated as HCl, multiply the acid number by .09115 to obtain percent HCl. For example; if the "acid number" is 0.80 on crude Aroclor, the corresponding HCl content is 0.8 x .09115 = 0.07 % HCl. The acidity may also be converted to HCl per million parts of Aroclor by multiplying the "acid number" by 911. For example, a distilled Aroclor having an "acid number" of 0.014 is equivalent to an HCl content of .014 x 911 = 12.7 parts HCl per million parts of Aroclor.

5. The acid number of distilled Aroclors should be less than .01.

6. Aside from free acid as a cause for NaOH consumption, ferric chloride which is usually present in small amount also consumes NaOH in neutralization to phenolphthalein. It

therefore follows that an Aroclor of very low acid number must be also extremely low in ferric chloride.

7. In the titration of crude Aroclors, if the black coloring matter obscures the phenolphthalein end point, add an equal volume of water and continue the titration. The water will not mix with the other liquids and the end point can be observed in the water.

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DETERMINATION OF SPECIFIC GRAVITY BY WESTPHAL BALANCE

GENERAL

Specific gravity is determined by means of the Westphal balance. The temperatures at which the specific gravities of liquid Aroclors are taken vary with the viscosity of the liquid. The specifications for each Aroclor should state the temperature for both the Aroclor and the water to which comparison of gravity is made. In plant practise, specific gravities of Aroclors containing up to 54% chlorine are made at 65°/65°C while specific gravities of Aroclors containing 60 - 62 % chlorine are made at 90°/90°C.

Specific gravities of any of the Aroclors may be made at 25°/25°C by use of the A.S.T.M. method for road tars, asphalt cements, soft tars pitches, serial designation D70-27, 1927 (described in Bureau of Standards Miscellaneous Publication No. 110, Standards and Specifications for Nonmetallic Minerals and their products, page 125.)

APPARATUS

Westphal Balance: Similar to Eimer and Amend Catalogue No. 16930. Plummet need not have thermometer scale to 90°C but should not be subject to injury by use at this temperature.

Cylinder: Pyrex glass hydrometer jar 1.5" x 6".

Thermometer: Use thermometer which has been checked for accuracy of scale in the range used.

PROCEDURE

Place the Westphal in such position that the plummet is 7 - 9 inches above the work bench. By means of the leveling screw, adjust the Westphal balance to show zero reading with a clean dry plummet in air. Suspend the plummet during adjustment in a empty cylinder to protect the apparatus from air currents.

Heat the Aroclor to be tested to a temperature about 15° higher than the temperature at which determination is to be made. For example, if specific gravity is wanted at 65°C, the Aroclor should be heated to about 80°C. Then pour the heated Aroclor into a clean Pyrex cylinder which has been warmed by setting at edge of hot plate. The cylinder should be filled with

the Aroclor to within about 1 inch of the top.

Allow the Aroclor in the cylinder to air cool until the temperature is about 7 degrees above that desired, then place the cylinder in a hot water bath which is at a temperature about 5 degrees above the desired temperature. A liter beaker containing sufficient water to be equal to or above the level of the Aroclor in the cylinder is a satisfactory water bath. In case the specific gravity is to be taken at 90°/90°, a glycerin bath should be substituted (glycerin bath should be substituted for the water bath to avoid the water vapor with its condensation on the Westphal balance which is present if water is used at high temperatures such as 95°C.

Without disturbing the adjustment of the Westphal which is set to read zero with plummet in air, place the cylinder containing the Aroclor in such position that the plummet is immersed in Aroclor and add weights to the beam of the Westphal until the beam is again level. The plummet should now be completely immersed as well as about 1/2" of the suspension wire and the plummet should not touch the cylinder at any point. Stir the Aroclor with a thermometer at frequent intervals until the desired temperature just is reached. At this point the weights are quickly adjusted until equilibrium is obtained and the reading noted.

Having obtained the reading for Aroclor at the desired temperature, the specific gravity is obtained by dividing this figure by the reading when the plummet is immersed in pure water at the same temperature. The reading for water is obtained in the same manner as for Aroclor. Since the reading for water is constant, provided there are no errors in weights or Westphal, this figure need not be determined with each Aroclor test. The figure for water which is used as a constant should, however, be checked once a month or whenever greatest accuracy is needed. The readings for water at 65°C and 90°C are respectively .9828 and .9672.

CALCULATION OF RESULT

Example 1. Assume readings as follows:

Westphal reading with plummet in air	zero
Westphal reading with plummet in Aroclor at 65°C	1.5025
Westphal reading with plummet in water at 65°C	.9828

Then sp.gr. at 65/65°C = $\frac{1.5025}{.9828}$ = 1.5288

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Example 2. Assume readings as follows:

Westphal reading with plummet in air	zero
Westphal reading with plummet in Arocolor at 90°C	1.5435
Westphal reading with plummet in Water at 90°C	.9672

Then sp.gr. at 90/90°C = $\frac{1.5435}{.9672}$ = 1.5958

NOTES

1. The weights used with the Westphal balance should be checked periodically by weighing each on an analytical balance.

2. The adjustment of the liquid to the exact temperature desired is most important. Do not allow to cool rapidly and stir frequently enough to maintain a uniform temperature from top to bottom in the cylinder.

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Fe in 1269 — 50 gm in 3" porcelain dish 10-15 cc 1:2 conc H_2SO_4 down to dryness on hot plt. - in muffle 15-20 min - cool - take up in conc HCl - reduce with $SnCl_2$ - cool - add - 8 cc CP H_3PO_4 - $HgCl_2$ - titrate $K_2Cr_2O_7$.

DETERMINATION OF IRON IN AROCLORS

Iron in Aroclors may be determined by extracting a benzol solution of the Aroclor with dilute hydrochloric acid until further extractions show no appreciable iron content. The iron in the combined extracts is then determined by the colorimetric method using potassium sulfocyanate.

PROCEDURE

The amount of sample taken is governed by iron content of the sample. The amount taken should be such that up to .0006 gm of Fe is present. The amount to be taken is indicated by the following table:

0.1	gram	sample	when	.3 to .6%	Fe	is	present	
.2	"	"	"	.1 " .3%	"	"	"	
.3	"	"	"	.05" .2%	"	"	"	
1.0	"	"	"	.01" .05%	"	"	"	
3 to 5	"	"	"	Below .01%				

The redistilled Aroclors are low in iron, consequently 3 to 5 grams sample should be taken. The black Aroclors usually contain .05 to .2% Fe, 0.3 gram sample is therefore used.

Transfer the weighed amount of sample to a clean separatory funnel of about 100 cc capacity. Add about 5 cc of benzol and shake until the sample is in solution. In the case of large amounts (3 to 5 grams) of sample the amount of benzol should be increased to about 10 cc to insure a solution of considerably lower specific gravity than the hydrochloric acid used for extraction.

When solution is complete, add 10 cc of 1:1 iron-free HCl and shake for about 2 minutes. Let stand until separation of the two layers is complete, then draw off and preserve the acid extract. Add another 10 cc of 1:1 HCl and shake again. Draw off the acid layer and combine with the first extract. Transfer the combined extracts to a Nessler tube and dilute with distilled water to about 90 cc. Add 10 cc of Normal KCNS solution and mix. Compare the color so obtained with the color of a standard solution made by adding standard iron solution to a Nessler tube containing 20 cc of 1:1 HCl, 65 cc of water, and 10 cc of KCNS solution. The standard iron solution is added from a burette until the color of the standard solution exactly matches the color of the sample.

The iron content in percent is found by multiplying the number of cc of standard iron solution required by the iron value of 1 cc of standard iron solution and by 100 and dividing by the weight of sample taken.

Example: If 6.0 cc of standard iron solution (1cc = .000053 gm. Fe) is required to match the color shown by 0.3 gram of sample, the iron content of the sample is 6.0 x .000053 x 100 divided by 0.3. The result is 0.106% Fe.

SOLUTIONS REQUIRED

Standard iron solution, 1 cc = about .00005 gram Fe. Reduce about 1 gram of ferric ammonium alum to a powder, mix well and transfer to a weighing bottle. Weigh by difference about 0.2 gram of sample into a 250 cc beaker. Add 100 cc of water and 25 cc of HCl. Transfer to a 500 cc volumetric flask, make up to volume, and mix well.

Weigh by difference another portion of about 0.2 gram ferric ammonium alum into a beaker and determine iron by ammonia precipitation and weighing the ignited oxide or by reduction of the iron in HCl solution with stannous chloride followed by titration against standard potassium dichromate, using diphenylamine as indicator. From the amount of iron found in the ferric ammonium alum the Fe value of the standard iron solution may be calculated. Ferric ammonium alum contains about 11.7% Fe. One cc of standard iron solution will contain about 0.00005 gm. Fe.

Potassium thiocyanate solution. Normal. Dissolve 100 grams KCNS in 1 liter of water.

Dilute hydrochloric acid, 1:1. The acid used should be free of iron. J. T. Bakers special HCl is suitable but should be tested to insure absence of iron.

NOTES

1 - Two extractions with 1:1 HCl has been found to remove the iron from the benzol solution with sufficient completeness. The completeness of extraction may be checked by making a third HCl extraction and by evaporating and igniting the benzol solution in a clean white porcelain dish. If the iron extraction is complete the dish should show no reddish brown iron stain after ignition.

2 - Acid extractions with dilute sulfuric acid are unsatisfactory due to a much greater number of extractions which must be made for complete removal of the iron.

3 - The red thiocyanate colors fade somewhat on standing. For this reason color comparisons must be made with freshly developed solutions and standards. In testing a number of samples, the extractions should be completed and the thiocyanate colors developed at one time. The samples can then be arranged in increasing color intensity and matched by adding standard iron solution from a burette to the single Nessler tube used for the standard solution.

4 - The volumes of the thiocyanate solutions at time of comparison should be approximately equal.

5 - Duplicate determinations on samples containing .05 to .20% Fe should agree within .02%.

6.- Results comparable with those obtained by acid extraction may be secured by carefully igniting the sample in a clean porcelain dish and dissolving the iron oxide residue in 20 cc of 1:1 HCl, then developing the thiocyanate color in the usual way.

7 - In case the Arocolor contains large amounts of iron (above 0.5%) the amount may be determined by titration of the HCl extract with 0.05 Normal potassium dichromate after reduction with stannous chloride. A sample of 2 to 5 grams may be used if the iron is to be determined by titration.

8 - Sulfocyanide forms the red color with iron in the ferric condition only. If ferrous iron is present it will not be shown by the sulfocyanide test. On account of the preparation of the Arocolors by chlorination, it may be assumed that iron present is in the ferric condition. The presence offerrous iron in the HCl extract may be tested for by addition of a solution of potassium ferricyanide to a diluted portion of the extract. If ferrous iron is present a blue color will develop. If ferroous iron is likely to be present in the acid extract, the extract should be evaporated to dryness after addition of a few crystals of sodium chlorate. The dry residue is then dissolved in HCl and treated with sulfocyanate in the usual manner.

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DETERMINATION OF FREEZING POINTS

The methods below are those recommended by the Research Department.

FREEZING POINT OF DIPHENYL

Sixty-eight to 70 grams of diphenyl are placed in a 100 cc Griffin-type beaker and heated to about 100°C. The beaker is then wrapped in a towel, making a loose layer of cloth about 2 inches thick around the beaker. The diphenyl is stirred with an Anschuetz (45 - 105° scale) thermometer and readings made every minute, until either the material is too solid to stir or until the bulb of the thermometer is exposed.

The observed temperatures are corrected for scale errors, if any, and plotted against time and a smooth line drawn through the points. The points will be found to form a two distinct curves which join at the point at which the diphenyl starts to crystallize. From the time crystallization starts until the material becomes practically solid there is a relatively slow temperature drop. This is known as the "hold" of the curve.

By definition, the freezing point of the sample of diphenyl will be the temperature at the arithmetical mean time of the "hold".

FREEZING POINT OF AROCLORS

For low-freezing materials such as Aroclor 1219, the recommended method is as follows:

Seventy cubic centimeters of Aroclor 1219 is placed in a 100 cc Griffin-type beaker. This beaker is placed in turn in a 150 cc beaker. The 100 cc beaker is supported by its flared rim on the rim of the larger beaker and hangs loosely in the larger beaker. The nested beakers are now placed in an ice sludge.

Initial Freezing Point. The Aroclor is stirred with an Anschuetz thermometer (scale 10 to 55°C). The temperature is read every minute and seeds of both 2-chlorodiphenyl and 4-chlorodiphenyl are added every minute until crystals begin to form in the liquid. The temperature at which crystals are

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first seen to appear is noted. Continue the stirring and temperature readings at one minute intervals until a thin slurry is obtained. In case supercooling takes place (as it often does), a temperature rise will occur after crystals have appeared. In this event, continue the stirring and temperature readings until two or three consecutive readings again show decreasing temperatures.

The highest temperature attained after crystals begin to appear is taken as the "initial freezing point". In case of no supercooling with resulant rise in temperature, the temperature at which crystals first appear is taken as the "initial freezing point".

Solidification Point. The 100 cc beaker is then removed from the larger beaker and placed directly in the ice sludge. Temperature readings are continued until the Aroclor becomes too thick to stir or until the bulb of the thermometer is exposed. The last reliable temperature is recorded as the solidification point.

Freezing Point. The freezing point of the Aroclor is arbitrarily taken as the average of the "initial freezing point" and the "solidification point". The "initial freezing point" and the "solidification point" should be reported along with the "freezing point".

Check. As a check on the initial freezing point the beaker may be removed from the ice sludge, warmed in the hand, while the Aroclor is stirred with the thermometer, until the temperature is 2° to 4°C. below the initial freezing point. The beaker is then wrapped in a towel and held in the hand. Stirring is continued until the crystals in the Aroclor just melt. The temperature at this point is recorded as the final melting point. If carefully determined, the final melting point serves as a check on the initial freezing point and should not differ by more than a few tenths of a degree at most from the initial freezing point.

If the melting point check is made, the average of the final melting point and initial freezing point is taken as the checked initial freezing point.

DSW 331922

NOTES

1. If carefully carried out and if the Aroclor is frequently seeded with both 2-chlorodiphenyl and 4-chlorodiphenyl, the determination of initial freezing point should not require checking by the melting point method. However, the Aroclor is very readily super-cooled so that unless great care

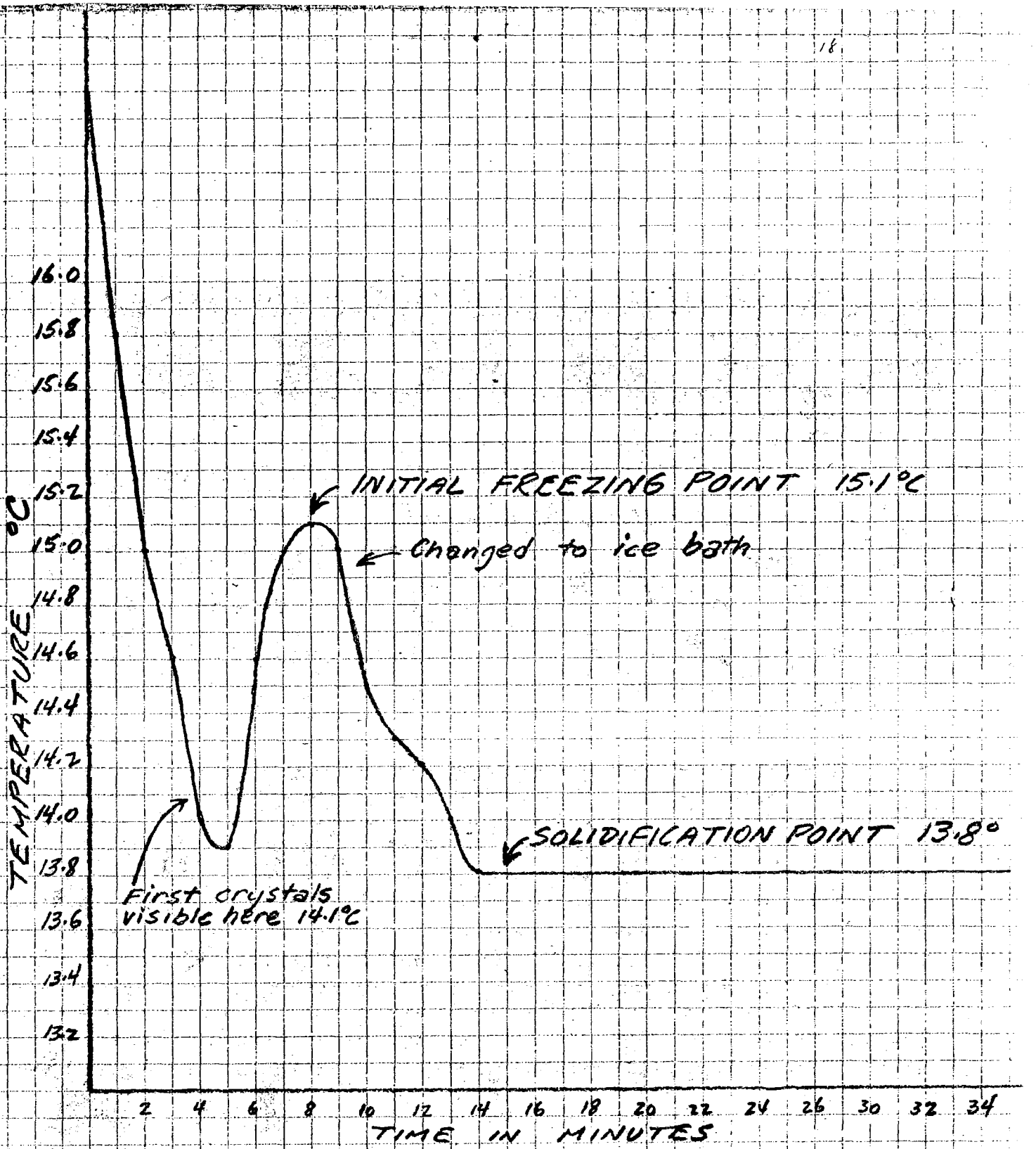
is taken, it may be cooled several degrees below its initial freezing point before crystallization starts. The result is that when crystallization does set in the temperature rises but the maximum temperature is not attained and observed intial freezing point is therefore low.

2. It is for this reason that the 100 cc beaker is jackedted with a larger beaker during the determination of the initial freezing point. The jacket serves to slow up the rate of cooling and insures a more accurate determination than the method where the 100 cc beaker is placed directly in the ice-sludge for the determination of initial freezing point.

3. On account of the short exposed mercury column of the Ansehuetz thermometers, corrections of observed temperatures for emergent stem are not ordinarily required. Under usual conditions of test, this correction is below 0.1°C. If conditions of test are such that the stem correction is large, the appropriate correction should be made and recorded as a corrected temperature. Scale corrections, if any, should always be applied.

4. In the determination, the stirring should be continous and the temperature readings made at one minute intervals throughout the test. The change from the water jacket to the ice bath should be made quickly without interruption of the one minute readings and the point of change to the ice bath should be indicated on the time temperature curve.

ABC/pw
9-5-30



TYPICAL FREEZING POINT CURVE FOR AROCLOR 1219

FREEZING POINT = 14.45°C (MEAN OF INITIAL FREEZING POINT AND SOLIDIFICATION POINT

DSW 331924

DETERMINATION OF BENZOL INSOLUBLE IN SOLID AROCLORS

PROCEDURE

Crush about 50 grams of resin. Weigh out 1 gram into a tared 125 cc flask, add 25 cc of benzol and agitate the flask with a circular motion for a few minutes. Then add 25 cc more of benzol, washing down the side of the flask. Allow to stand for 1 hour.

Prepare a #3 Gooch crucible with an asbestos pad in the usual manner and dry to constant weight. Arrange the crucible for filtration by suction.

Filter the solution through the crucible, using slight suction. Use about 50 cc of benzol to transfer the insoluble material left adhering to the sides of the flask and to wash any adhering film of resin from the sides of the crucible. Dry the crucible and flask in an oven at 105 - 110°C, cool and weigh.

Add to the weight of the insoluble material in the crucible any insoluble matter remaining in the flask. Report insoluble matter as percentage of original weight of resin taken.

NOTES

1. The method described above is the one used by the H. H. Robertson Company.

ABC/pw
9-5-30

VAPORIZATION LOSS AT 66°C

The test below is that given to us by the H. H. Roberston Company. They call for the 100 hour loss at 150° F (= 66°C).

PROCEDURE

Melt slightly more than 50 grams of Aroclor in a suitable container, being careful not to raise the temperature higher than necessary to make the resin fluid. Pour into a tared shallow glass container (100 millimeter Petri dish), cool to room temperature and weigh.

Heat for 100 hours (4 days, 4 hours) at 66°C, in a drying oven provided with a venting outlet for escape of volatile matter. Remove from the oven, cool to room temperature and reweigh. Report loss in weight as percentage of original weight.

NOTES

1. On account of the small vaporization loss at 66°C, the weights must be taken very carefully. It is very important in obtaining these close weights that the dish and contents be at atmospheric temperature when the weights are taken.

2. Robertson's first description of this test called for the determination of loss after 50, 100, and 150 hours of drying. From this data, they drew up curves showing loss against time. Their latest procedure calls only for the loss on 100 hours drying.

ABC/pw
9-6-30

DIPHENYL IN CRUDE DIPHENYL OR DIPHENYL STILL BOTTOMS

PROCEDURE

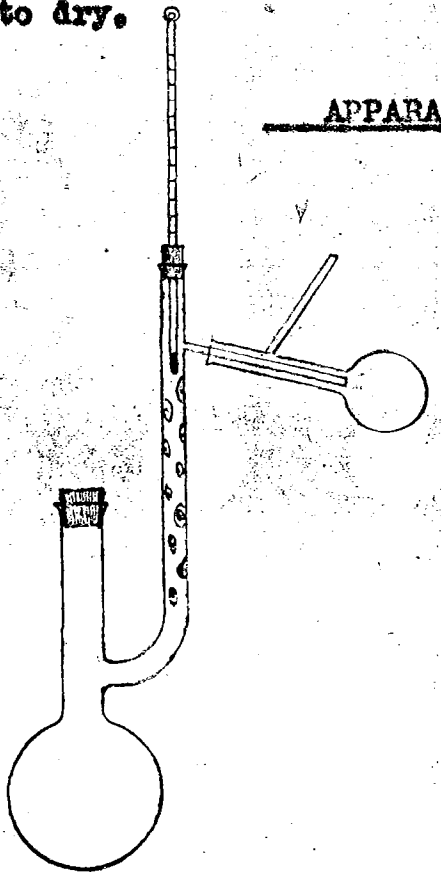
Transfer 100 to 200 grams of the sample to a 250 cc beaker. Weigh beaker and contents on a rough balance to nearest gram. Warm beaker until contents are liquid then pour 100 to 150 grams into a 250 cc distilling flask with 10 inch distilling column attached. Reweigh beaker and contents, thereby obtaining by difference the weight of sample used.

Place a 300°C or 400°C thermometer in the top of the 10 inch distilling column in such a way that the top of the bulb is even with the bottom of the side neck outlet. Distill off the diphenyl and collect in a weighed receiving flask until the thermometer reads 275°C. Weigh the receiving flask again and calculate results.

$$\% \text{ diphenyl} = \frac{\text{wt. diphenyl} \times 100}{\text{wt. of sample}}$$

Pour the residue in the flask while still liquid into a casserole or pan kept for this purpose. Rinse with benzol and allow to dry.

APPARATUS



The distilling flask is a 250 cc flask to which a 10 inch column with side outlet near top is attached. The column has indentations to increase surface area. Asbestos paper should be wrapped around the column.

A Meker burner is used in heating the flask. Since a high boiling point must be reached, the transite board or wire gauge on which the flask rests should have a hole nearly as large as the diameter of the flask. The flame may also be applied directly to the flask without the use of any transite board or wire gauge. If necessary, asbestos paper should

be placed at the top of the flask.

A 100 cc distilling flask makes a convenient receiver for the distillate.

ABG/pw
9-5-30

MAGNESIUM CARBONATE TEST

This test was furnished us by the H. H. Robertson Co. Heat 25 grams of Arocolor in a 100 cc beaker to 150°C. Add 1.4 grams of pure magnesium carbonate and stir until the mixture is homogeneous, keeping the sample at 150°C. Pour into a clean 3 inch tin top and allow to cool. Compare color with the standards furnished us by the H. H. Robertson Company.

APPEARANCE

The specifications on each Arocolor should state what examination is to be made for appearance, color, sediment, structure, etc.

ABG/pw
9-8-30

CORRECTIONS FOR THERMOMETER READINGS

References: Circular 8,
Bureau of Standards, The
Testing of Thermometers.

Thermometers are tested and scale corrections given for total immersion because this is a definite basis to which observations taken with any known distribution of temperature along the stem can be referred. If tests were made in a given depth of immersion and room temperature, the results would not be applicable when the thermometers were used in a different bath at a different room temperature, even though the depth of immersion remained the same.

EMERGENT STEM CORRECTION

In general, all corrections are determined for total immersion, that is, for the condition where both bulb and stem of the thermometer are at the same temperature. If, however, the stem is emergent into space either hotter or colder than the temperature of the bulb, a stem correction must be applied to the observed reading of the thermometer.

This so called stem correction is very large if the number of degrees emergent and the difference of temperature between the bath and space above it are large. It may amount to more than 20°C for measurements made with a mercurial thermometer at 400°C.

FORMULA FOR STEM CORRECTION

The stem correction may be computed from the following formula:

Stem correction = K x n(T - t)

K = factor for relative expansion of mercury in glass; 0.00015 to 0.00016 for centigrade thermometers, average value 0.000155

n = length, expressed in degrees, of the mercury column emergent from the bath.

T = observed thermometer reading.

t = mean temperature of the emergent stem

(measured by a second thermometer which is fastened by means of rubber bands to the thermometer measuring the bath and the bulb of which is at the middle of the exposed thread of mercury).

Example No. 1. Suppose that the observed temperature was 100°C and the thermometer was immersed to the 20° mark on the scale, so that 80° of the mercury column projected into the air, and the mean temperature of the emergent stem colume was found to be 25°C, then:

$$\text{Stem correction} = 0.000155 \times 80 \times (100 - 25) = 0.93^\circ C$$

As the stem was at a lower temperature then the bulb the thermometer read too low, so that this correction must be added to the observed reading to find the reading corresponding to total immersion.

Example No. 2. Suppose that the observed reading was 500°C and the thermometer was immersed to the 100° mark, so that 400° of the mercury column projected out into the air; the mean temperature of the emergent column was found to be 150°C, then the approximate value of the stem correction = $0.000155 \times 400 \times (500 - 150) = 21.7^\circ C$.

The approximate temperature of the bath is consequently $500^\circ + 21.7^\circ C. = 521.7^\circ$. A closer approximation to the true value of the stem correction is given by substituting the corrected bath temperature, i.e., 521.7°C in the formula thus:-

$$\text{Stem correction} = 0.000155 \times 400 \times (521.7^\circ - 150) = 23.0^\circ C.$$

Note: Where the thermometer passes thru' a cork as in a distillation set-up, the degrees emergent should be computed from the center of the cork.

SCALE CORRECTION

Scale corrections are determined by direct comparison against a thermometer which has been calibrated by the Bureau of Standards. Each thermometer used for the accurate determination of boiling or freezing points should be carefully compared at full immersion with a standard thermometer and a record made of the corrections which must be made at many different points on the scale.

The data may be kept as a table or as a curve. The scale corrections must, of course, be well established at the temperature points at which the thermometer will be chiefly used.

Since thermometers may change due to exposure to heat or to the slow natural contraction of the glass which may continue for years, restandardization of the thermometer are required from time to time.

BAROMETER CORRECTION

The temperature of boiling liquids and consequently that of its vapor varies with the atmospheric pressure.

For the boiling point of water, the correction of atmospheric pressure can be obtained by adding 0.0375°C for every mm. the prevailing barometric pressure reads below 760 mm or subtracting 0.0375°C for every mm. above 760 mm. For example, if the observed temperature reading is 99.4°C at a barometric pressure of 744 mm., the corrected temperature is 99.4 + (16 x 0.0375) = 100.0°C.

For the boiling points of liquids other than water, the correction factors may be calculated approximately if the vapor tension at the boiling point is known. For example, for benzol the correction factor per mm. of pressure is 0.043°C, for xylol the correction factor per mm. is 0.052, for turpentine the correction factor is 0.056°C. Mulliken "Identification of Organic Compounds" gives 0.036°C as an average correction figure which can be used on organic liquids.

In the case of the boiling point and distillation range of Aroclors where the temperatures are high and the correction factor is unknown, it is advisable to omit correction for barometer. The barometric reading, however, should be recorded along with the distillation or boiling point data.

ABG/pw
9-2-30