forces contribute greatly to the ultimate properties of the polyester urethane elastomers. Modulus apparently is affected primarily by intermolecular attractions at high $\bar{M}_c$ values, and by primary cross links at low $\bar{M}_c$ values.

Temperature dependence of the torsional modulus of elastomers cross linked with trimethyolpropane [3-(hydroxymethyl)-1,5-pentanediol] was also determined. Figure 7 shows the Clash-Berg torsional modulus for a series of Multrathane XA–trimethylolpropane cured elastomers. The modulus of a specimen containing no cross linking through triol extension, curve 1, was highest but fell off rapidly at 130° to 150° C. When 70% of the diol extender was replaced with the triol, curve 2, the room temperature modulus was lower but did not exhibit a significant decrease until a temperature of 170° to 190° C. had been reached. Complete substitution of triol for diol resulted in a still further extension of the temperature at which loss of modulus occurred (curve 3). This may be explained by the fact that hydrogen bonding and van der Waals forces are more readily disrupted by thermal means than is primary valence bonding. Where the hydrogen bonding and van der Waals forces were present in the greatest amount, as for curve 1, a material stronger and harder at room temperature was obtained, although its thermal stability was not as great as was that of the triol cross-linked elastomers. While the foregoing explains to a large extent the reasons for improved thermal stability of the polymers containing more cross linking obtained from the triol, it does not appear to be a complete explanation. Part of the improvement is believed due to the greater thermal stability of the urethane linkages (in the triol cross link) compared to that of the allophanate cross link (*6*).

As expected, increases in the degree of cross linking shifted the glass transition region somewhat toward higher temperatures.

ACKNOWLEDGMENT

The assistance of T.H. Cleveland and C.D. Nolen in preparing the polyesters used in this study is gratefully acknowledged.

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Urethane Polyether Prepolymers and Foams

Influence of Chemical and Physical Variables on Reaction Behavior

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"A New Process Control for Making Polyether Urethane Foams" by these authors appears in the July 1960 issue of *Industry and Engineering Chemistry* on page 613.

Three other articles from the May 1959 meeting of the Division of Rubber Chemistry appear on pages 605 to 612 of the July *I/EC*.

OVER THE LAST several years the urethane idustry has seen a major shift in emphasis from polyester-based foams to polyether or polyglycol systems. This has led to successful production techniques for manufacturing flexible and rigid polyether urethane foams and elastomers primarily through trial and error procedures. Reproducibility of the chemical and physical properties of raw materials and their consistency in polymerization have been of prime importance to the industry. The Raw Materials Subcommittee of the Society of Plastic Industry (SPI), Cellular Products Division, has sponsored test methods which have been accepted by ASTM (*1*) and data-exchange programs on a continuing basis in recognition of this need. In addition, raw material suppliers have introduced formulations and technology regarding processing conditions for prepolymer and one-shot techniques for urethane foam manufacture. The prepolymer method lends itself more readily to quantitative reaction rate determination and the conclusions of this study can be applied directly to this technology. By extrapolation, one-shot techniques warrant similar scrutiny.

Factors considered as affecting polyether prepolymer technology are outlined in Table I. Process refinements have materially improved the chemical and physical characteristics of both the polyglycols and aryl diisocyanates currently in use, particularly with respect to water content and unsaturation level of the polyol. The latter is

Table I. Factors Considered in Evaluation of Prepolymer Reaction

Raw Materials	Conditions
Polyglycol	Hydroxyl number, pH, water content, unsaturation, alkali metals as sodium and potassium, carbonyl, saponification value, and total chloride
TDI	Total hydrolyzable chloride, % isomer ratio, and assay
Process conditions	Temperature, reactor design, OH/NCO ratio, agitator design and r.p.m., purging technique, and absence of air or moisture

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hypothesized to be terminal unsaturation and an indication of undesired monofunctionality. With water content now well below 0.1% by weight and unsaturation below 0.04 meq. per gram in polyethers of about 1000 molecular weight units per hydroxyl unit, it is not felt these factors seriously affect prepolymers for foam production. Reasonable accuracy in determining these values as well as the hydroxyl number (*1*) leaves little need for extensive investigation in this area. On the other hand, pH, alkali metals, carbonyl, saponification number, and total chloride content of polyglycols have been under frequent study with no reported conclusions at this writing as to their influence on prepolymer and foam preparation. Data from this study were also negative, in that no correlation was found between these values and prepolymer behavior. Process conditions as outlined are critical, however, and will be related to the conclusions of this study later. Furthermore, it has been found that the toluene diisocyanate now produced commercially is substantially lower in total hydrolyzable chloride than a year ago and continues to maintain its isomer ratio and assay values.

Bradley, Kogon, and Kane (*3*, *4*) and Heiss and others (*2*) have found the urethane reaction to be sensitive to basic substances (*3*). These substances have been empirically controlled to date by the addition of hydrochloric acid, benzoyl chloride, or other hydrolyzable organic chlorides (*5*) to the toluene diisocyanate (TDI) component where laboratory control checks on new lots of raw materials showed prepolymer reactivity greater than desired for plant operation. Because polyglycols are known to be base-catalyzed during manufacture, considerable emphasis has been given to controlling pH on the acid side and keeping alkali metals content at low levels to minimize basicity. This has prevented the problems of a "run-away" reaction or gelation of prepolymer batches which plagued the industry a year or more ago. Yet variations in prepolymer reaction behavior and foaming characteristics were still not entirely eliminated, nor was ideally consistent proccessing achieved.

This article presents the net CPR value, or controlled polymerization rate concept, as a means towards this goal. By reproducible quantitative analyses, trace components in the polyglycol and TDI can be determined and an optimum net catalytic balance obtained for any prepolymer reaction. The CPR factor of the polyglycol represents residual weakly basic constituents not qualitatively defined, but including weak acid salts of strong bases present in the less than 10-p.p.m. range. A certain amount of this catalytic activity is desirable to achieve reasonably short prepolymer processing time in production. This level is represented as net CPR, or the difference between the CPR of the polyglycol and the immediately available or active hydrolyzable chloride present in the TDI used. This value will vary and has been found to be less than but otherwise unrelated to the total hydrolyzable chloride now commonly determined. The remaining hydrolyzable chloride not initially neutralizing the reserve basicity of the polyether does evidently take part in the prepolymer foaming and curing steps where tertiary amine catalysts are employed.

Polyglycol — Toluene Diisocyanate (TDI)

CPR = reserve basicity

Net CPR = CPR − AHC_1

AHC_1 = active hydrolyzable chloride

AHC_2 = lesser active hydrolyzable chloride

THC = total hydrolyzable chloride by Society of Plastics Industry method or $AHC_1 + AHC_2$

Table II and Figure 1 outline briefly the method for determination of the CPR value, whereas Table III briefly outlines tecnhiques for determining AHC_1, THC, and AHC_2 by difference. Complete descriptions are in the section on analytical procedures.

In relating the significance of these tools to prepolymer processing, Figure 2 shows a fairly typical viscosity development curve where second-stage addition of TDI is employed. This technique is usually made to encourage allophanate branching reactions for good foaming without sacrificing linear polymer development necessary for high elongation, and resiliency in the final foam. For subsequent data, reaction rate of a given system is taken as the time necessary to reach point *A* in Figure 2 of 150 centipoises at 120° C. reaction temperature or 10,000 centipoises at 25° C.

Table II. Outline of CPR Determination for Polyglycols

Factors	Amounts or Methods
Sample	30 grams of polyglycols
Solvent	100 ml. of methanol
Titration	Potentiometric pH titration with 0.01*N* HCl
End point	Detected as inflection point on pH curve
CPR value	Ml. 0.01*N* HCl × 10

In Figure 3 data are shown where the active hydrolyzable

Table III. Outline of Determination Made on Toluene Diisocyanate and Their Relationships

Determination	Titration	Terms Reported
Active hydrolyzable chloride		
10 ml. TDI 100 ml. 1-propanol	As ml. 0.01*N* $AgNO_3$ to millivolt inflection point	Ml. × 2.63 = AHC_1
Total hydrolyzable chloride		
SPI analysis	As 0.01*N* $AgNO_3$	Ml. × 2.63 = THC

AHC_2 = THC − AHC_1 and THC = $AHC_1 + AHC_2$

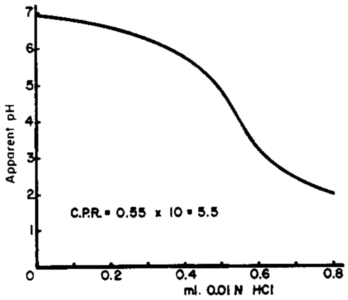

Figure 1. Example of CPR titration curve

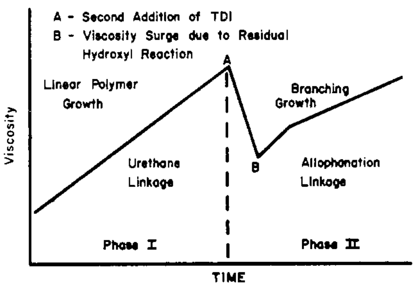

Figure 2. Prepolymer viscosity development

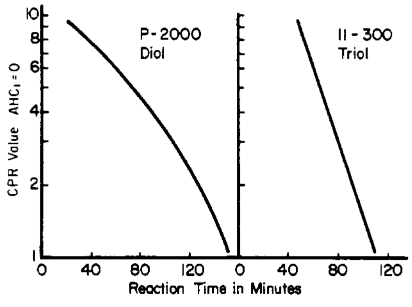

Figure 3. Influence of CPR of polyol on reaction rate with AHC of TDI constant

chloride of the TDI used was zero. Here the net CPR value of the system equals the CPR of the polyglycol. Both diols and triols of the polyoxypropylene type experience marked changes in reaction time with the relatively slight differences in reserve basicity of the system. This potent catalytic effect carries through to production scale equipment.

The influence of net CPR on the reactivity of the system is approached in Figure 4 from the other direction by using TDI of varying AHC_1 values with the same lot of polyol. Again, the reaction time required is increased as the net CPR decreases. These data are presented on linear coordinates to show the effect of a negative net CPR, or an excess of AHC_1. Essentially no further increase in reaction time is experienced with incremental quantities of AHC_1 after all the polyol CPR has been neutralized.

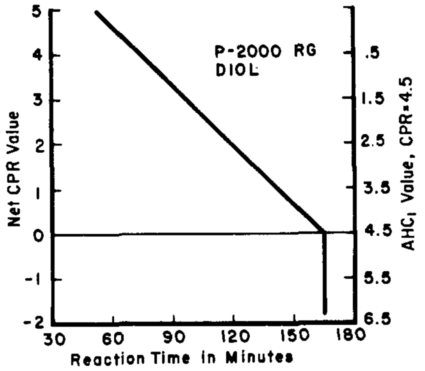

Figure 4. Influence of AHC_1 of TDI on reaction rate with CPR on polyol constant

The influence of net CPR would appear a simple arithmetic relationship, except that the AHC_1 value does not remain constant through the course of phase I polymerization, as AHC_2 is plainly neutralizing the system during the entire processing of the system. Several representative TDI samples are plotted in Figure 5 and show the effect of temperature and presence of weak acid salts, two conditions of the urethane reaction. The effect on polymerization behavior is noted in Figures 6 and 7. Although a significant factor to consider, increase in AHC_1 during the urethane reaction should not cause serious problems in employing the net CPR technique. Peculiar performance from time to time could be spot-checked by the method outlined in Figure 4 and compensation in process time made accordingly.

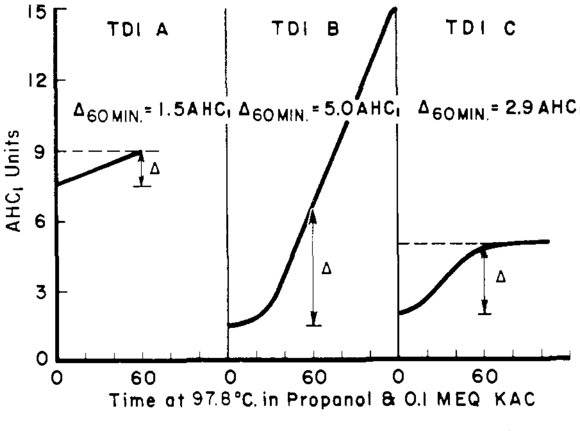

Figure 5. Increase in AHC_1 with temperature and basicity

The prepolymer viscosity development curve is shown in Figure 2, where the phase II or branching growth portion of the curve warrants investigation in the light of these developments. Figure 8 shows that below a threshold net CPR level of less than 0.4 unit no significant branching-type polymerization occurs.

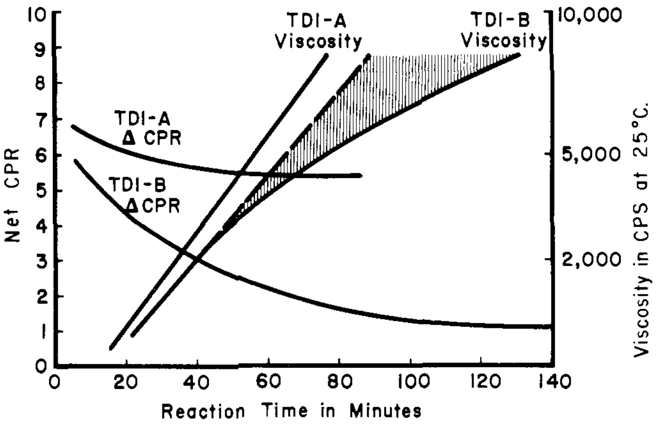

Figure 6. Influence of AHC_1 increase on viscosity development

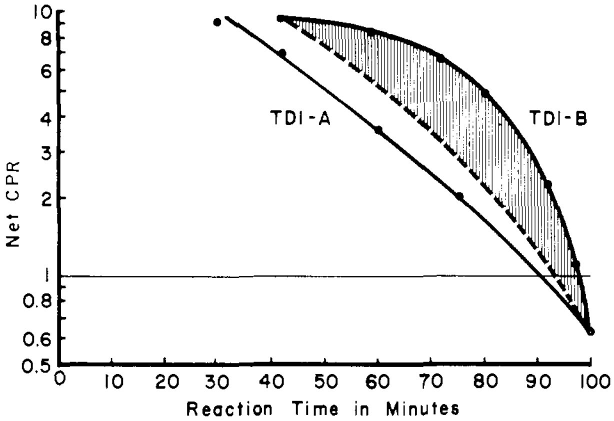

Figure 7. Influence of AHC_1 increase on reaction time of various polyglycols

The essentially urethane reaction behavior of phase I is compared with the essentially allophanate reaction behavior of phase II and is shown in Figure 9.

Other factors in the polyglycol, including saponification value, total chloride, pH, and carbonyl value, have been examined exhaustively and no significant correlation with prepolymer reaction behavior has been observed. In summary, the significant variables affecting prepolymer processing are hydroxyl number, water content, unsaturation, and CPR of the polyol and isomer ratio, and AHC_1 of the diisocyanate. The net CPR relationship, or CPR of polyol minus AHC_1 of TDI, should provide a major tool in achieving optimum and reproducible processing conditions.

The equipment used in the laboratory studies was a monitoring device that controls and records temperature,

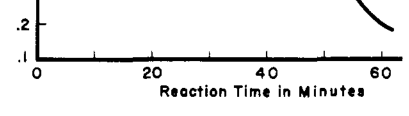

Figure 8. Influence of net CPR on reaction time of branching growth

while at the same time recording viscosity continuously at reaction temperature. The latter values are immediately converted to 25° C. values when desired. The reaction times established at this scale correlate well with plant production at the 500- to 2000-gallon level as shown in Figure 10. Each production facility must be spot-checked in building up the relationship shown, because of variations in individual reactor design, agitator speed, and efficiency of nitrogen blanketing of the surface of the reactants.

Processing variables of importance are reaction temperature and NCO/OH ratio. Figure 11 shows deviations from normally expected viscosity growth in the linear phase at temperatures well in excess of 104° C. The critical threshold appears between 130° and 140° C. as shown in Figure 12. The reaction kinetics evidently favor allophanate branching at this temperature level. The further limitations of NCO/OH mole ratio to reaction temperature in maintaining the foam properties attributed to essentially linear prepolymers is shown in Figure 13.

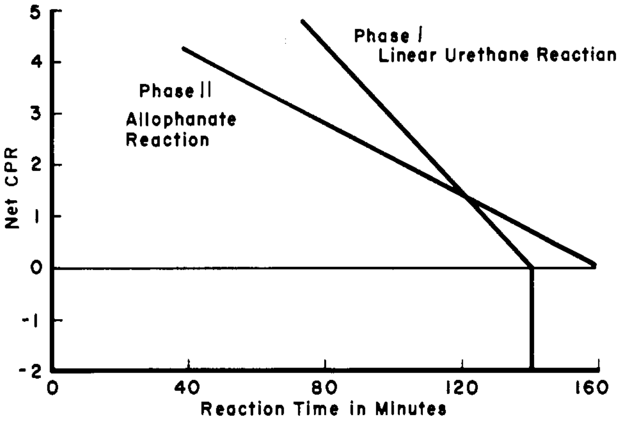

Figure 9. Net CPR of varied polyols and TDI systems affecting reaction time of phases I and II

A capsule summary of foam properties that may be expected with varying viscosity build-up rates is shown in Figure 14. The prepolymer systems are carried through polymerization phases I and II prior to foaming. Inadequate viscosity development without appropriate urethane (or linear) and allophanate (or branching) development leads to foam collapse, whereas excessive viscosity build-up probably due to excessive branching polymerization in the foam, leads to poor elongation, high hysteresis, and low tensile strengths in the foam.

The advent of one-shot technology makes reaction control even more critical, inasmuch as the forms of polymer growth described here take place in seconds rather than hours. Net CPR factor techniques are now being studied in this area. The direct conversion of reactants to foams complicates quantitative studies, but empirical results so far look encouraging though not conclusive.

In conclusion, the net CPR factor relationship now available to the urethane industry can be readily calculated from data based on a group of accurate and reproducible tests applied to the polyglycol and diisocyanate raw materials. The net CPR factor singularly influenced viscosity development of prepolymers on a consistent and reproducible basis. This and the other methodology described can provide a technological framework for producing specific and predictable prepolymers and foams.

ANALYTICAL PROCEDURE

CPR VALUES of POLYGLYCOLS

Scope. This procedure is used to determine the CPR (controlled polymerization rate) value of the polyglycols used in the manufacture of polyurethanes. The CPR value defines quantitatively the weakly basic materials present in the polyglycols, which act as catalysts in the polymerization of the polyglycol with the diisocyanate. The catalysts present are not defined qualitatively, but are determined

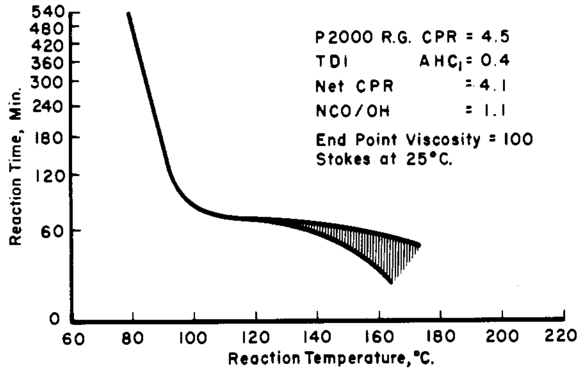

Figure 12. Linear polymerization reaction time vs. temperature

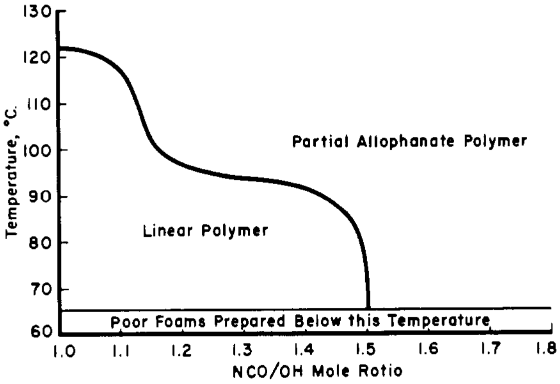

Figure 13. NCO–OH mole ratio and reaction temperature relationship to prepolymer development

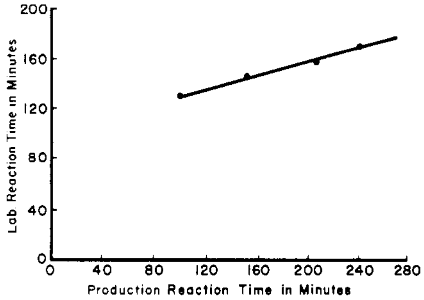

Figure 10. Correlation of Laboratory reaction times with production reaction times

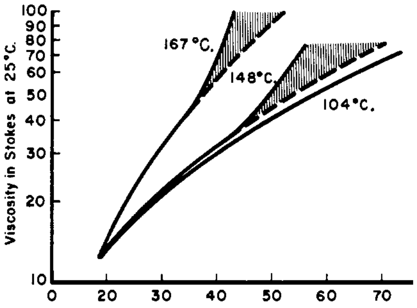

Figure 11. Linear or phase I polymerization at varying temperatures

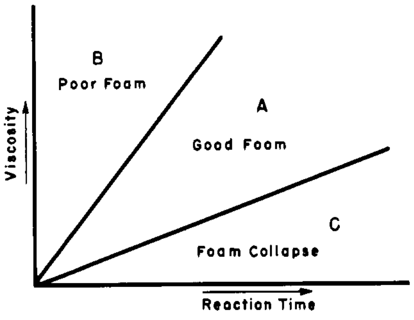

Figure 14. Reaction time vs. viscosity relationship and effect on foam properties

as the total weak acid salts of the strong bases, alkali metal, and alkaline earth weak acid salts. This method is not applicable to the amine-initiated type polyglycols in defining active catalysts present.

Principle. A large sample of the polyglycol is dissolved in reagent grade methanol and titrated with a very dilute, strong acid, the course of the titration being followed potentiometrically by using a pH meter.

Apparatus. Beckman Model G pH meter or equivalent instrument. Calomel sleeve-type electrode. Glass electrode. Buret of 2- or 5-ml. capacity. Magnetic stirrer and stirring bar.

Reagents. 0.01*N* standardized aqueous HCl. Reagent grade methanol (Baker's analytical reagent grade or equivalent).

Procedure. METHANOL BLANK. (a) Standardize the pH meter with aqueous pH 7 buffer, using the sleeve-type calomel and glass electrode system.

(b) Pipet 100 ml. of reagent grade methanol into a throughly cleaned 250-ml. beaker which has been rinsed with distilled water.

(c) Place the beaker with methanol on the magnetic stirrer, add the stirring bar, insert the electrode system, and start stirring.

(d) Titrate the methanol with 0.01*N* standardized aqueous HCl, adding increments of 0.02 to 0.05 ml. from a 5-ml. buret, titrating to an apparent pH of about 2. Record the pH after each incremental addition of reagent.

(e) Prepare a graph, plotting milliters of 0.01*N* HCl *vs.* pH. Take the end point of the titration as the mid-point of the pH inflection curve. Figure 15, curves *A* and *B*, represent the blank titration of two different lots of methanol. The blank titration should be less than 0.2 ml. of 0.01*N* HCl.

SAMPLE. (a) Weigh a 30 ±0.1-gram sample of the polyglycol into a throughly cleaned 250-ml. beaker which has been rinsed with distilled water.

(b) Add 100 ml. of reagent grade methanol using the 100-ml. pipet.

(c) Place the beaker and contents on the magnetic stirrer, add the stirring bar, and insert the electrode system.

(d) Start the magnetic stirrer and titrate the system with standardized aqueous 0.01*N* HCl, adding increments of 0.02 to 0.05 ml. from a 5-ml. buret. Titrate to an apparent pH of about 2.5. Record the pH after each incremental addition of reagent.

(e) Prepare a graph, plotting milliters of 0.01*N* HCl *vs.* pH, using the mid-point of the pH inflection curve as the end-point of the titration. Figure 18, curves *C* and *D*, represents two different lots of polyglycol. Subtract the methanol blank from the sample titration, to obtain accurate results. Wash the electrodes with methanol after the titration is completed.

Calculation.

$$CPR = (B - A) \times 10$$

ACTIVE HYDROLYZABLE CHLORIDES IN TOLUENE DIISOCYANATE

Scope. The hydrolyzable chloride found in commercial toluene diisocyanate can be classified into two types. To distinguish these types, one is defined as the active hydrolyzable chloride (AHC_1) and the other as total hydrolyzable chloride (THC). The former is in a form such that it will immediately neutralize weakly basic substances present in polyglycols, while the latter is the total of all hydrolyzable chloride present. The ASTM procedure, which requires solution of the diisocyanate in methanol, followed by the addition of water, and a prolonged hydrolysis at elevated temperature, determines the total hydrolyzable chloride.

Principle. Two methods can be used for the determination of AHC_1 chloride. In the first method, the diisocyanate is dissolved in reagent grade propanol and titrated potentiometrically with standardized, dilute silver nitrate. In the second procedure, the AHC_1 chloride is measured as the loss in basicity of a standardized nonaqueous dilute weak acid–strong base salt solution. Both methods are extremely accurate; duplicate titrations generally do not vary by more than 0.01 ml. of 0.01*N* reagent. These two methods give results which are always in close agreement, whereas they may differ drastically from the THC value.

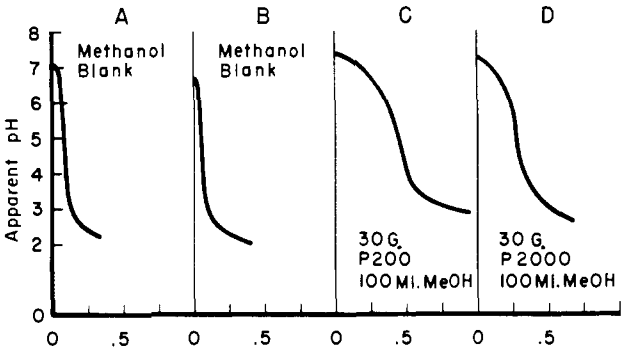

Figure 15. Potentiometric curves for CPR

DIRECT SILVER NITRATE TITRATION

Apparatus. Potentiometer, Beckman Model G pH meter or similar type instrument with potentiometric scale. Silver–silver chloride electrode with potassium sulfate salt bridge (Fisher Scientific Co., No. 9-312-38 or equivalent). Silver electrode (Fisher Scientific Co., No. 9-312-37 or equivalent). Buret of 10-ml. capacity, graduated in 0.05-ml. divisions. Magnetic stirrer and stirring bar.

Reagents. Standardized aqueous 0.01*N* $AgNO_3$. 1-Propanol (Eastman Chemicals.,No. 848 or equivalent).

Procedure. 1-PROPANOL BLANK. (a) Place a thoroughly clean, 250-ml. beaker containing a stirring bar on a magnetic stirrer and pipet 100 ml. of 1-propanol into the beaker.

(b) Turn on the stirrer and add 2 drops of concentrated nitric acid to the beaker.

(c) Immerse the silver–silver chloride and silver electrodes in the propanol solution and adjust the pH meter to the millivolt scale.

(d) Titrate the solution with the 0.01*N* $AgNO_3$, adding increments of 0.05 ml. of reagent from a 10-ml. buret. Record the millivolt reading after each addition of reagent.

(e) Plot millivolts *vs.* milliliters of reagent added. Take the end point of the titration as the mid-point of the potentiometer curve. In Figure 16, *A* shows a typical blank titration of 1-propanol.

SAMPLE. (a) Proceed as in (a) above.

(b) Turn on the stirrer, pipet 10 ml. of toluene diisocyanate sample into the beaker, and add 2 drops of concentrated nitric acid.

(c) Proceed as in (c, d, and e) above. Figure 16, curve *B* shows a titration curve for AHC_1 chloride in a commercial toluene dissocyanate sample. Subtract the 1-propanol blank titration from the sample titration to arrive at the accurate result. The values for AHC_1 chloride vary from zero to about 150 p.p.m.

AHC_1 CHLORIDE VIA BASICITY LOSS METHOD

Apparatus. Same as that used for direct silver nitrate titration.

Reagent. ≈0.001*N* potassium acetate in 1-propanol (Potassium or sodium salts of bicarbonate, monohydrogen phosphate, or other weak acids can also be used.) Standardized 0.01*N* HCl.

Procedure. STANDARDIZATION OF 0.01*N* POTASSIUM ACETATE–1-PROPANOL. (a) Standardize the pH meter by using pH 7 buffer solution.

(b) Place a thoroughly clean 250-ml. beaker containing a stirring bar on a magnetic stirrer and add 100 ml. of potassium acetate in 1-propanol reagent with the 100-ml. volumetric pipet.

(c) Turn on the stirrer and immerse the sleeve-type calomel and glass electrodes into the solution.

(d) Titrate the solution with the 0.01*N* HCl, adding increments of 0.05 ml. near the end point. Record the pH after each incremental addition of reagent.

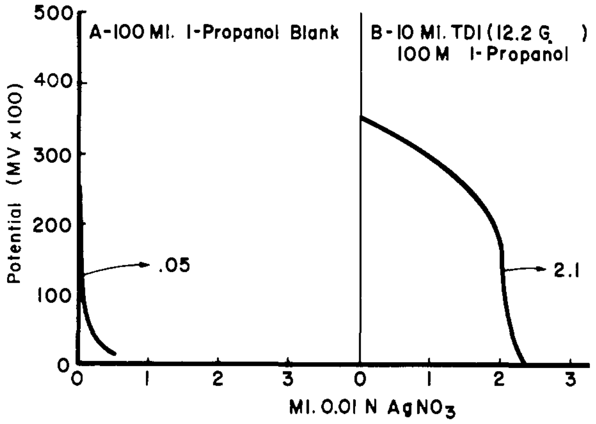

Figure 16. Potentiometric curve for AHC_1 direct titration

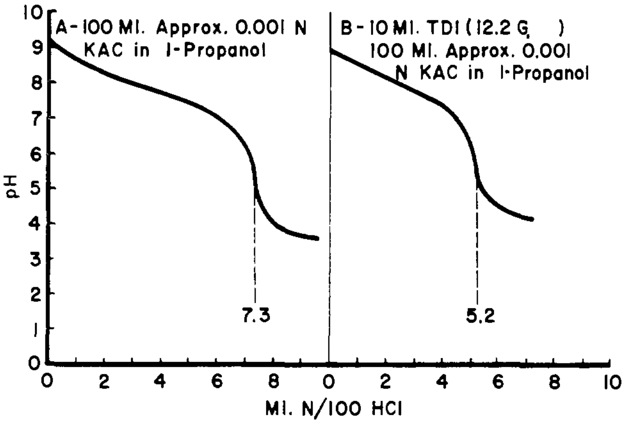

Figure 17. Potentiometric curve for AHC_1-basicity method

(e) Prepare a graph as in the direct silver nitrate titration. Curve *A* in Figure 17 shows the result of the standardization of the potassium acetate–propanol reagent.

SAMPLE. (a) Proceed as in (b) above.

(b) Turn on the stirrer, add 10 ml. of toluene diisocyanate to the solution with the 10-ml. volumetric pipet, and immerse the calomel sleeve-type and glass electrodes into the solution.

(c) Proceed as in (d and e) above. Figure 20, curve *B*, shows the results of the titration for the same toluene diisocyanate sample as used for the direct silver nitrate method.

Calculation.

$$\text{Cl, p.p.m.} = \frac{(A - B) \times 355}{12.2}$$

ASTM METHOD FOR TOTAL HYDROLYZABLE CHLORIDE

Scope and Application. This method is intended to determine the hydrolyzable chloride content of refined toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, or mixtures of the two. The main sources of hydrolyzable chlorine in the isocyanates are carbamyl chloride and dissolved phosgene. Both compounds are reactive with alcohols and water, forming ureas, carbamates, carbon dioxide, and hydrochloric acid. The method may alos be applied to other isocyanates of suitable solubility.

Summary of Method. The isocyanates react with methanol, forming carbamates, and the hydrochloric acid liberated is absorbed in water. The carbon dioxide bubbles off during the reaction. The chlorides absorbed are then determined potentiometrically using a standardized silver nitrate solution.

Interferences. Thiocyanate, cyanide, sulfide, bromide, iodide, or other substances capable of reacting with silver ion as well as substances capable of reducing silver ion in acid solution interfere with the determination.

Apparatus. Weighing bottle or any device suitable for weighing a liquid sample by difference to the nearest gram. Any heater-stirrer unit that will accomodate a 400-ml. beaker. A potentiometric titrator similar to the Fisher Scientific Co. Titrimeter, or the Beckman Model K automatic titrator if many samples are involved. Silver–silver chloride and silver electrodes as used in direct silver nitrate titration.

Reagent. $0.01N$ $AgNO_3$ standardized frequently enough to detect changes of $0.0005N$ either gravimetrically or potentiometrically using standardized HCl.

Procedure. (a) Weigh, by difference, 10 ±1 grams of sample into a clean, dry 400-ml. beaker. If the hydrolyzable chloride content is expected to be less than 0.01%, use 20 ±2 grams of sample.

(b) Add 50 ml. of methanol by means of a graduate, and stir.

(c) Continue stirring until the reaction starts—indicated by the warming of the beaker and crystal separation on the sides of the beaker). Then add distilled water to fill the beaker half full. Continue stirring during this addition of water. The water must be added quickly to prevent hard solidification of the reactants and to minimize any loss of hydrochloric acid. Some isocyanates will not react readily and slight warming might be necessary to initiate the reaction. Other isocyanates may react, as noted by the warning of the reactants, but may not form a crystalline mass.

(d) After adding water, boil gently for 30 minutes with continual agitation. (Use stirrer-heat units).

(e) After digestion, wash down the sides of the beaker with distilled water. Remove and wash the stirrer. Cool the beaker and solution in an ice bath. When it is cooled to approximately 10° C., add 10 drops of concentrated nitric acid.

(f) Titrate potentiometrically with $0.01N$ $AgNO_3$ using the Fisher Titrimeter (or equivalent instrument) with silver–silver chloride and silver electrodes.

(g) Add the $0.01N$ $AgNO_3$ in small increments, noting milliliter and millivolt readings after each addition. If there is little or no change in millivolt readings, increase the amount of silver nitrate addition. If the chloride content appears to be very high, that is greater than 0.2%, use $0.1N$ $AgNO_3$ instead of the $0.01N$ $AgNO_3$.

(h) Record each volume with its particular millivolt reading, until at least 3 ml. are added well past the point of noticeable change in the dial reading, usually over 0.200 mv.

(i) Construct a curve by plotting volumes on the abscissa and millivolt readings on the ordinate.

(j) The end point is the point of inflection (middle of break) of this curve. Then drop a perpendicular to the abscissa to obtain the volume at the end point.

Calculation. Calculate the hydrolyzable chlorine as follows:

$$\%\ \text{hydrolyzable chlorine} = \frac{\text{ml. } AgNO_3 \times N \times 3.546}{\text{weight of sample}}$$

where N = exact normality of the silver nitrate solution.

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