

Continuously Recording Viscosity

Reprint 102

Instrumentation for Continuously Recording Viscosity of Resins and Polymers in Large Reactors at Processing Temperatures

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In the last few years the resin and polymer production methods have changed from small batch kettles to large several ton capacity reactors. Since this change, many attempts have been made to devise a simple but rapid and accurate method of tracing the size of the polymer particle through its processing cycle to completion of polymerization to a previously determined point. Up to this time resin manufacturers have not had a rapid, continuous and reliable test method for materials at processing temperature which have the properties of a variable, rapid and critical increase of polymerization, and which may go to an insoluble and infusible stage before an operator realizes the necessity of corrective measures.

This project was organized to study available instruments which would resolve a solution of this important control phase of resin and polymer manufacture in large reactors at processing temperatures. It is not expected that the continuous viscosity recording type of control instrumentation will entirely replace tests normally used to indicate the end point of polymerization, although with some experience it probably could be refined to reach this point.

One of the most used and important methods of determining polymer size is to obtain the viscosity of a solution of the material. Let us review for the moment the scientific basis for viscosity. Viscosity is defined as that property of a liquid that resists flow at any velocity, however small. The basis for

calculations is: If you have a true mobile liquid (Newtonian liquid) such as water or mineral oil placed between two parallel plates and move the top plate at a constant velocity, each layer of molecules moves with velocity directly proportional to its distance from the stationary plate. This, interpreted into a formula is: Viscosity equals shear stress divided by rate of shear and is termed absolute viscosity, the unit of which is expressed by poises. Since a polymer with a large molecular weight becomes less soluble and immobile, it follows that its shear stress will be greater and can be determined by viscosity.

Many methods have been devised to measure viscosity, some of which are as follows:

1. Timing measured amounts through a standard orifice exemplified by the Ford and Universal Viscosity Cups.
2. Number of revolutions per second of a paddle, a certain area of which is inserted in the material to be tested, and driven by a known torque weight, such as the modified Stormer Viscosimeter.
3. The deflection of a spring wire with a plummet or paddle attached at one end and inserted into the liquid and on the other end is fastened a constant speed motor and an indicating scale and pointer. The Mac Michael and Brookfield Viscosimeters are examples of this type.
4. By a standard size and weight metal sphere, timed as it falls a

calibrated distance through a solution or the solution is forced upward against a plummet in a graduated glass tube. The Fisher-Porter and Norcross Viscosimeters are examples of this type.

5. Standard comparator tubes depending on the rate of rise of an air bubble in a calibrated glass tube, such as the Gardner-Holdt viscosity system.
6. Super-sonic wave energies vibrated in a liquid and translated to poise by electronic devices, such as the viscoson.

Many plastics and resin solutions which are manufactured for surface coatings are thixotropic; therefore, give false viscosity results when measured by the foregoing methods. Thixotropic liquids (non-Newtonian liquids) are those which decrease in viscosity as the rate of shear increases.

One simple hypothesis which has been used to explain the difference between Newtonian liquids and non-Newtonian liquids, or thixotropic liquids, is that the Newtonian liquids arrange themselves as spherical particle between shear surfaces, while the non-Newtonian liquids have irregular molecular shapes; such as egg shape, which when stirred or sheared rapidly will assume a spherical shape.¹

These facts may explain some of the peculiar viscosity results indicated by instruments used and reported on in this paper. Potential thixotropic effects have not been established as highly influential on viscosity of resin

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liquids at high processing temperatures, but unaccounted for variations, in graphed viscosity curves have been observed.

A few of the various instruments and methods devised to determine viscosity, especially for use in the varnish, resin and polymer industry are:

1. The Gardner-Holdt Bubble Tube Method
2. Cure Plate Method
3. Melting Point
4. For Viscosity Cup or Saybolt Universal
5. Zahn Cup
6. String from a hot spade used to stir the varnish in a kettle
7. Brookfield Synchro-lectric Viscosimeter

The Cure Plate, the Zahn Cup, and a string from a hot spade are rather crude, but rapid tests of viscosity. The more accurate methods require 15 minutes or more and are much too slow for accurately measuring viscosity of rapidly polymerizing materials.

The instruments applied to this problem which is essentially measuring polymer size at processing temperatures by viscosity measurements are as follows:

1. The Brookfield Synchro-lectric Viscosimeter² based on a plummet fastened to a spiral spring wire, the other end of which is attached to a constant speed synchronous motor.
2. General Electric Thermal Converter³ to measure very accurately the power consumed by the motor on the large agitators used in resin and polymer reactors.
3. The Fisher-Porter Flow Tube Viscorator⁴ which measures shear

at fixed pressure and flow through a calibrated tube containing flow and viscosity sensitive floats.

4. The Norcross Viscosimeter⁵ based on timing a falling plummet through a liquid.
5. The Rich-Roth Ultra Viscoson⁶ based on the rate of vibration of super-sonic waves passed from one segment to another segment of a probe immersed in a liquid.
6. Strain Gauge Method.⁷

Factual Data

The Brookfield Synchro-lectric Viscosimeter

The Brookfield Synchro-lectric Viscosimeter, being of a design for only laboratory use, was tested by bodying varnish linseed oil in a stainless steel beaker at 560°F. The instrument was included in this report to determine whether this type of measuring principle might be re-designed to be applied to large processing vessels.

The instrument was fastened in a level and rigid position over a 2000 ml beaker of varnish linseed oil. The oil was heat bodied at 560°F to a Z₃ Gardner-Holdt viscosity.

The Brookfield was set at 60 rpm, using a number one spindle. It was allowed to run one minute before each reading, and a reading was taken every one-half hour during the processing of the oil.

The viscosity variation between raw linseed oil and Z₃ bodied linseed oil at 560°F is very small and a much more sensitive spindle should have been used to bring the indicator into a higher range. *Figure 1* shows a graph of the viscosity as indicated by the

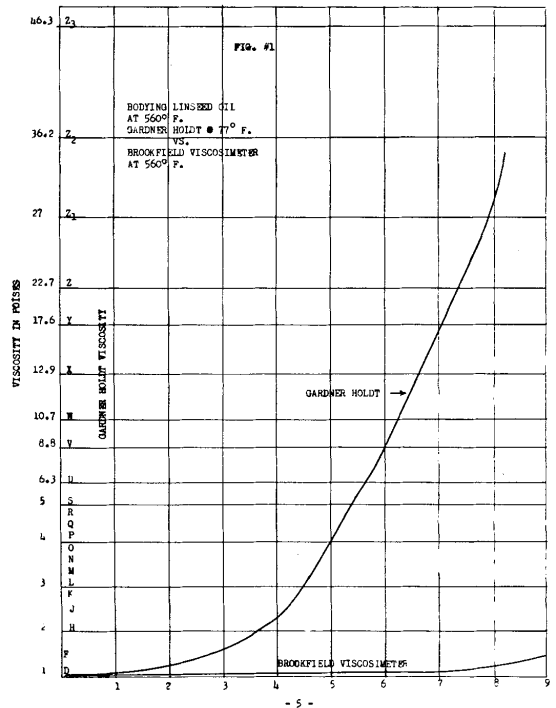


Figure 1

Brookfield Viscosimeter at 560°F and compared with the Gardner-Holdt scale in stokes at 77°F.

The lower guide bearing of the Brookfield instrument has a large clearance, and allowed fumes from the oil to get into the working parts, which caused a slightly sticky action of the indicator toward the end of the cook. The instrument is well designed for laboratory testing at room temperature; but for determining the viscosity of hot sticky resins in large, heavy, industrial equipment an ingenious design would be required for permanent attachment to record viscosity continuously.

The General Electric Lincoln Thermal Converter

A two horse power motor was attached to a Reeves varispeed transmission, which was in turn attached to a 24" turbine with blades six inches

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wide, inclined 45° in a 1250 gallon resin reactor. Carbon dioxide was introduced through the resin mass by means of holes drilled in the underside of a circular pipe placed at the lower outside perimeter of the turbine.

The approximate speeds of the agitator shaft at gauge settings on the varispeed transmissions were as follows:

- Gauge Setting No. 2 Position- 45 rpm
- Gauge Setting No. 3 Position- 63 rpm
- Gauge Setting No. 4 Position- 81 rpm
- Gauge Setting No. 5 Position- 100 rpm

Readings of the Brown continuous recording instrument for number of amperes drawn by motor were as follows:

- Recorder reading of 150 motor drew 3.3 amps
- Recorder reading of 200 motor drew 4. amps
- Recorder reading of 250 motor drew 5. amps
- Recorder reading of 290 motor drew 5.6 amps
- Recorder reading of 300 motor drew 5.8 amps

The power required at any given speed with the Reeves drive, with inert gas off, and any given resin formula was approximately in direct proportion to the speed of the turbine, 45 rpm to 100 rpm.

This method of recording viscosity was affected too greatly by the amount of CO₂ blown into the batch. It was observed that when more carbon dioxide was blown into the batch, a relatively lower power reading would be recorded, due to the gas being distributed in small bubbles in an

increasing number through the varnish mass, which in turn would lower agitation energy. With carbon dioxide flowing at a constant rate all through the processing period of a high end point viscosity resin polymer, there was a variation of only 4% of the recording scale to show the viscosity increase. Even this line was not a clear cut and definite recording.

Figure 2A shows a graph of this method of viscosity recording while processing a short oil alkyd having an end point viscosity T-U Gardner-Holdt scale.

After trying different horse power motors and other methods of making the instrument more sensitive to viscosity increase without success, the method was abandoned as not being practical.

The Fisher Porter Viscorator

The Fisher-Porter Viscorator records viscosity continuously by forcing a liquid, at constant flow and temperature, upward through a vertical, conically tapered, graduated glass tube containing two floats. The bottom float is sensitive to flow and is used to keep

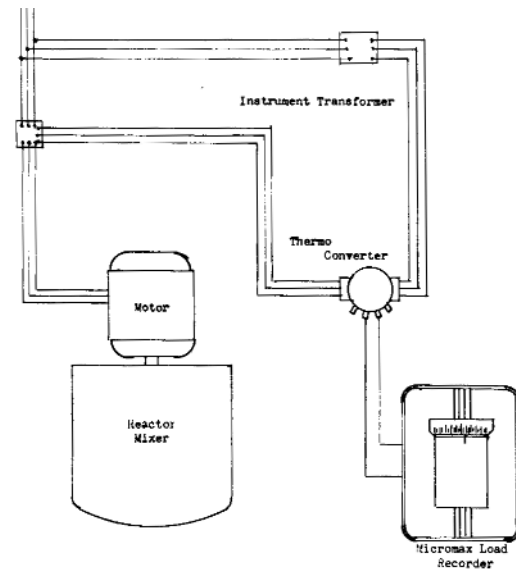


Figure 2

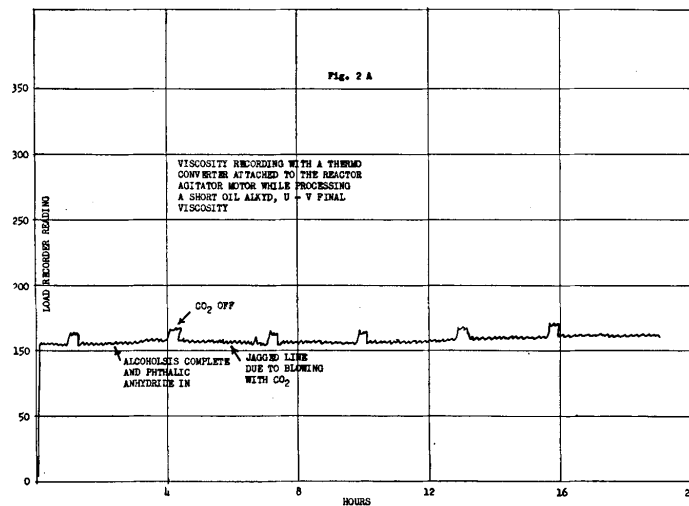


Figure 2A

the flow rate constant, while the top float is sensitive only to viscosity. As the viscosity of the fluid increases it forces the viscosity sensitive float gradually upward along the graduations of the glass tube from which readings are taken.

A pump with a by-pass on the discharge side drew the hot resin from the resin reactor and forced it through the viscorator and back to the reactor. The

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flow rate at processing temperature was regulated by the by-pass valve. Two connections were placed in the system to circulate cleaning fluids such as fatty acids, solvents, etc.

It was very difficult to get a pump which would circulate the hot resin through the system properly. The hot resin caused the newer pumps to seize, due to heat expansion of metal parts circulating the hot resin. It was often difficult to get the pump to start the flow of resin through the system if it was cold and the resin had polymerized to a high viscosity. A well worn pump was then tried and some success was obtained in the proper circulation of the hot resin.

After the resin is circulated through the viscorator and the viscosity starts to register nicely, skins start passing between the metering floats and the tapered glass tube walls. In a short time the floats began to stick to the glass tube and become insensitive. Screens were placed over the intake pipe to the pump, but this did not seem to eliminate the trouble with small gel particles.

The small inert gas bubbles would collect into a large bubble and this would also upset the flow and the action of the plummets.

These difficulties seemed to reoccur regardless of the precautions taken to prevent them, and further work was discontinued.

Indications are that if it were not for pump trouble and skin formation through the system this method would give very accurate results.

It is believed that if a more satisfactory method of circulating hot resins through the system could be

designed, the instrument could be adapted to determine viscosity at high temperature.

The Norcross Viscosimeter

The Norcross Viscosimeter is designed to determine viscosity by measuring the time it requires a plummet to fall through a tube of material to be tested. It is a very simple rugged instrument and can be designed with little difficulty to be used in large reactors with full vacuum or high pressure, which is necessary for manufacturing certain resins and polymers.

The plummet is enclosed in a long stainless steel tube which is fastened into the top of the processing vessel near the outer perimeter by a flanged connection. The tube must be out of reach of agitators and foam whips and be well braced in an absolute plumb position so that large pieces of hard resin being thrown about by the agitator would not dislocate it or throw it out of plumb. The bottom of the tube must be immersed 12 to 14 inches in the molten resin, and within the tube, the plummet must be completely submerged the total distance of its movement. The resin slowly flows through the holes in the side of the lower end of the tube so that the liquid in the well is representative of the batch at all times.

A motor driven cam raises the plummet and then releases it to fall through the molten resin to the bottom of the tube. The time required for the plummet to fall through the resin is recorded each three minute period on a

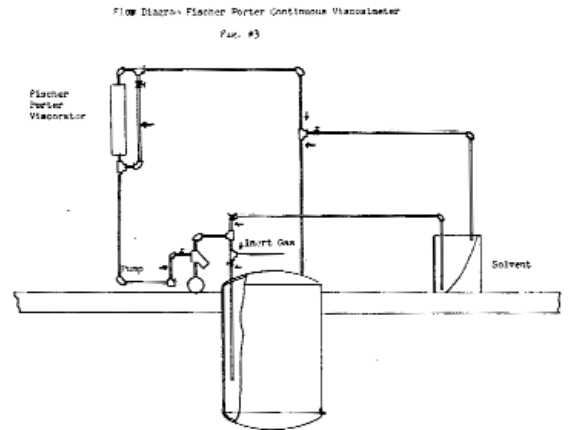


Figure 3

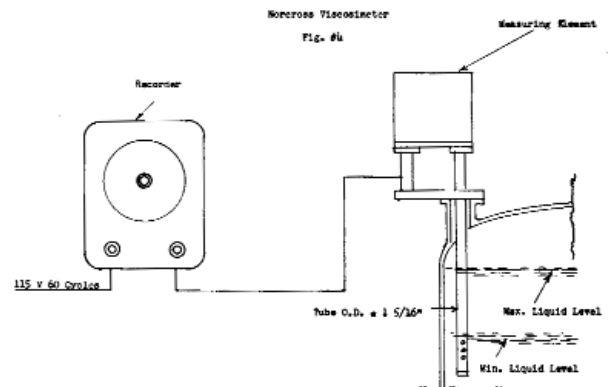


Figure 4

recorder dial, graduated from zero to one hundred. Although the graduated scale does not record viscosity in poises, one of several plummets having sensitivities of two tenths to two thousand poises is selected for molten resin, so that the recording on the graduated scale will not be above 80 points of the dial.

Members of the committee have had the instrument in operation for nearly a year. In some instances the operators of the resin reactors have indicated that they can determine at what point the resin has reached the designated pre-determined end point of polymerization, as indicated by either cure test or the solution viscosity,

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Gardner-Holdt method. This is especially true where one batch after another of the same composition and viscosity end point are being processed. The molten resin must be controlled within five to six degrees during the processing cycle to make the recorder curves coincide closely for the same material. Four to five batches of resins have been made consecutively without cleaning the equipment and without fouling the viscosimeter with skins to the extent it would not register properly.

The instrument is equipped with an alarm to warn the operator of any build up of viscosity which exceeds the setting of the instrument. Corrective measures can be taken at this point to stop the resin from going to the insoluble and infusible stage.

Figures 5 and 6 show graphs of batches of a medium oil phthalic alkyd, a short oil, maleic hardened ester gum varnish cooked in situ.

The square drawn at the end of graph curves is established end point variation which can be tolerated to pass either a cure check or Gardner-Holdt viscosity standard.

The Rich-Roth Ultra Viscoson

This instrument showed sufficient results on the first test to warrant further investigation, which is going on at the present time.

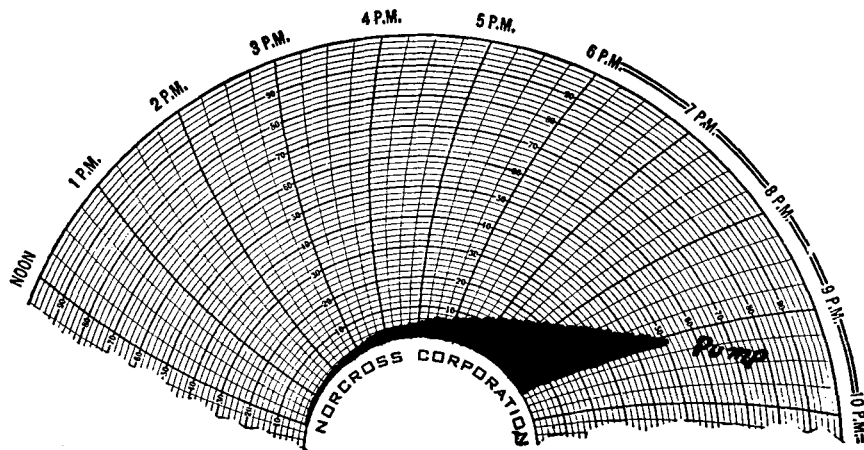
The instrument is an electronic type instrument that measures change of energy imposed by supersonic electrical waves as they vibrate in a small probe immersed in the resin or polymer. The energy change is recorded electrically directly in poise viscosity units.

In the use of the instrument for control of processing resins, satisfactory duplicate results were not obtained from batch to batch. Indications are that the instrument's performance is very sensitive to slight changes of the processing environment.

The results of the recordings suggest that when approximate duplicate readings are obtained that the scale changes can be expected as follows:

Forty per cent of scale on high viscosity short oil alkyd resins. Eight per cent of scale range on long oil alkyd resins. The amplitude of temperature change approximating eight degrees at processing temperatures varies the recorder 3% of the scale.

After the manufacture of 10 or 12 batches of resin, either electronic or probe trouble developed and the recordings became erratic and did not



Batch A—No. 739 Piston (see also Figure 5)

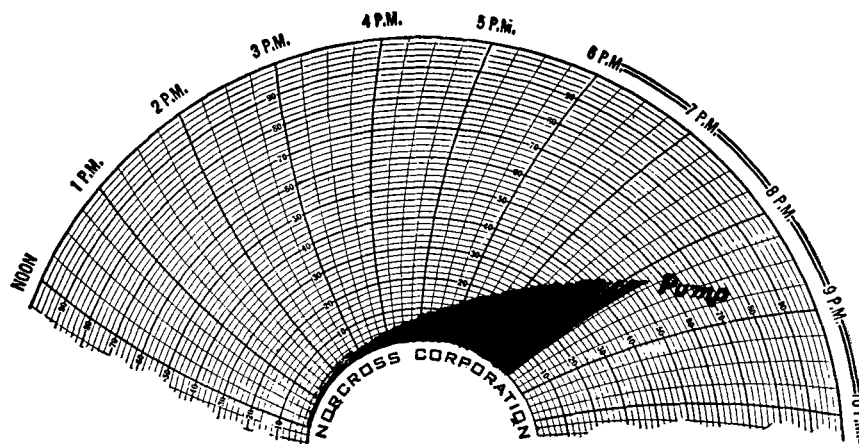


Figure 4A - Reprints of Norcross continuous viscosity recordings of Batch A and D at 446°F to 454°F using a No. 739 piston. The illustrated curves indicate the extent of variation recorded by the Norcross Viscosimeter of the maximum and minimum viscosity of a series of the same varnishes processed and terminated to achieve end point Gardner-Holdt viscosity.

Figure 4A (See also Figure 5)

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repeat itself on batches of the same formulation.

The instrument has been returned to the manufacturer for adjustment. Further tests will be run when it is returned.

Figure 7 is a graph of the results of the three batches of a medium long oil alkyd processed consecutively.

Figure 8 is a graph of two batches of a short oil alkyd. The results were somewhat erratic.

The Strain Gauge Method for Determining Viscosity

The Strain Gauge is constructed of two lead wires fastened to two or three "U" turns of fine wire of known electrical resistance, which are cemented with plastics to a flexible spring steel flat bar. One end of the flat bar is fastened to a shaft which is driven by a constant speed synchronous motor. At the other end a paddle is attached which is immersed in the molten resin. The two electrical wires on the bar are brought out through the hollow drive shaft and connected to take-off rings. Two brushes conduct the electrical impulses from the revolving rings to the stationary Strain Gauge Recorder⁸. As the viscosity of a material increases, strain on the bar of the revolving paddle increases, and causes the steel bar to bend slightly. This slight bend of the bar increases resistance of the fine wire "U" turns and is recorded by the Strain Gauge recorder. However, the Strain Gauge must be insulated from heat, corrosive fumes, and friction to record viscosity with precision.

A small laboratory assembly of the instrument in a beaker of varnish which was being processed, recorded

continuous change of viscosity satisfactorily.

Since there were no manufacturers of instruments to record viscosity by this method, no further experimental work was carried on.

Discussion

Any viscosity or viscosity measuring instrument is read or recorded at a specific temperature, and in case the varnish or polymer is in solution, readings are made at definite non-volatile content in specified solvents.

When recording viscosity at processing temperatures, any fluctuation of temperature will immediately be recorded in terms of viscosity by the instrument. Therefore, when comparing Gardner-Holdt viscosity with those of continuous recording instruments, the assumption must be made that all batches and samples on which viscosities are being determined are held at exactly the same temperature and that each batch of the series will be held at exactly the same temperature as is possible. It must be assumed that all sample reductions were reduced accurately to 50% non-volatile matter in the specified thinner and read correctly at 77 degrees (77°)F against standard Gardner-Holdt

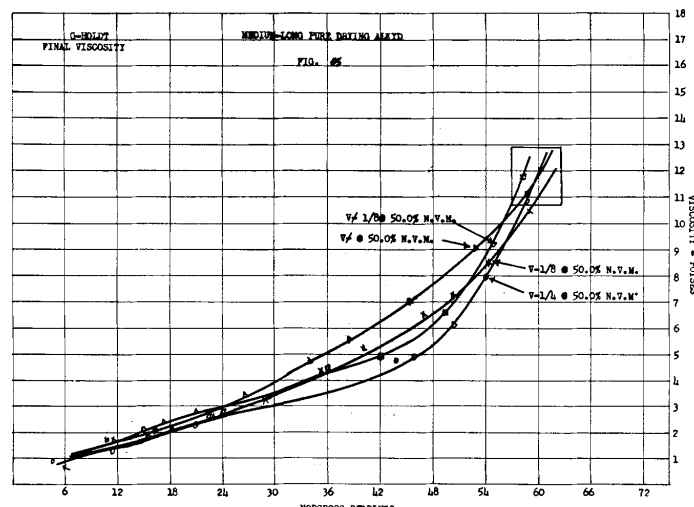


Figure 5

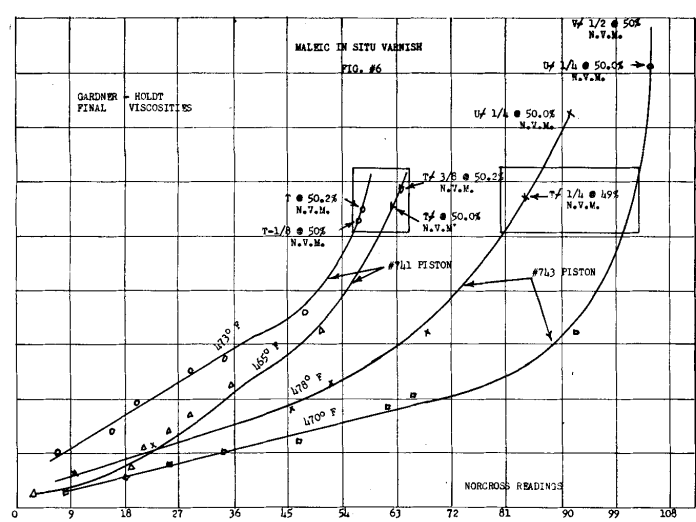


Figure 6

viscosity tubes.

In lieu of these factors, when using continuous recording instruments such as the Norcross, certain facts immediately become evident. The widest extreme of the graph (see Figure 5) occurs with viscosity of 5 poises at 25°C and at 50% NVM in mineral spirits. Batch A shows a Norcross reading of 35, while Batch D shows a reading of 46½ for the same Gardner viscosity in stokes.

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There is a *maximum* of 11½ numbers on an instrument arbitrarily calibrated to read between 0 and 100. Probably a better method of expressing this relationship is in terms of the maximum spread in viscosity for any one Norcross reading. The maximum spread in viscosity occurs at a reading of 48. Batch A has a viscosity of 7.7 poises at 50% NVM in mineral spirits, corresponding to a U + ½ on the Gardner-Holdt tubes. Batch D, with the same Norcross reading, has a viscosity of 5.32 at 50% NVM in mineral spirits corresponding to T - 1/8 on Gardner-Holdt tubes. This is not too great a spread for Gardner-Holdt viscosities and Norcross reading 53, 54, 55 and 56 points, at which the batches left the reactor, gave end point viscosities which were within specifications designated by the limits enclosed by the outlined square.

Although many factors are involved, all must be considered, such as small variation in solids on the solution used to pre-determining viscosity and variation in Norcross reading at the time the batch left the reactor to come within the specification.

Table A gives the approximate toler-

Table A - Norcross Readings

Viscosity Gardner-Holdt	N.V.M.	Batch A			Batch B		
		Low	High	Span	Low	High	Span
W-X	50.0%	57	62½	5½	59	61	2
W-X	49-51%	53	64	11	55	62	7

Table B - Norcross Readings

Viscosity Gardner-Holdt	N.V.M.	Batch A			Batch B		
		Low	High	Span	Low	High	Span
S-U	50.0%	56	60	4	60	64½	5
S-U	49-51%	45	63	19	52	68	14

Table C - Norcross Readings

Viscosity Gardner-Holdt	N.V.M.	Batch A			Batch B		
		Low	High	Span	Low	High	Span
S-U	50.0%	81	87	6	98	101	3
S-U	49-51%	70½	92	21½	90	103	13

ance of these variations.

The nature of the curve of Batch C is such that its high and low Norcross readings would allow all batches to meet the viscosity and N.V.M. requirements for the alkyd; a span of 7 units.

The Norcross instrument is designed to use various sizes of pistons to cover all ranges of viscosity from .2 centipoise to 200,000 centipoises.

Figure 6 shows the effects of using two different pistons on the same batches of alkyd. Batches A and B incorporated No. 741 piston, and Batches C and D a No. 743 piston.

When processing maleic varnish in situ, the rapid and variable

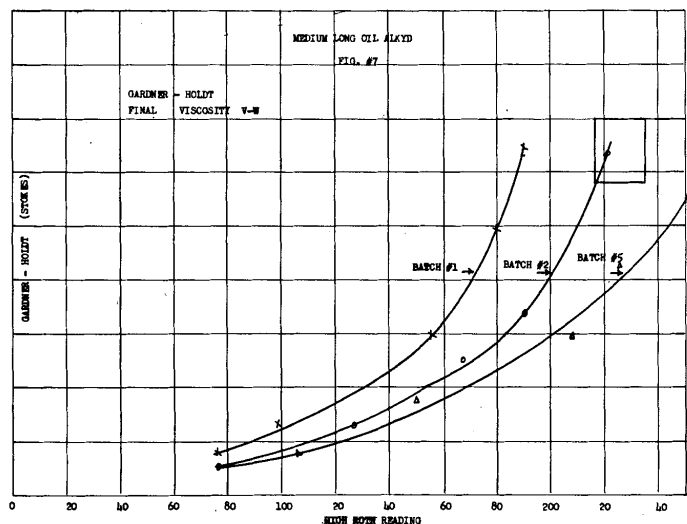


Figure 7

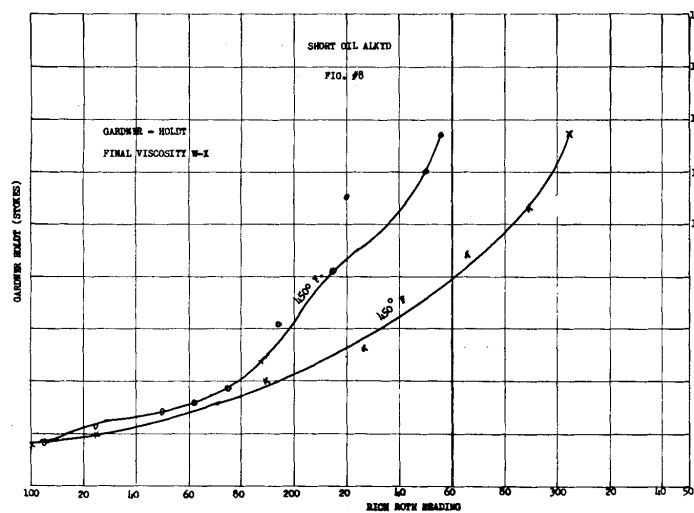


Figure 8

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rate of polymerization requires the operator to vary the temperature somewhat to control the speed of reaction. As is shown in *Figure 9*, a variation of 465°F to 475°F with a No. 741 piston will vary the Norcross reading 2 to 3 numbers, and the same variation with a No. 743 piston causes the reading to vary 9 to 10 numbers.

Tabulation of the tolerance permitted by the Norcross Viscosimeter for maleic varnish processed *in situ* is given in *Table B*.

By taking the highest Norcross reading of Batch A and the lowest reading of Batch B, we find that a span of 11 numbers will give the desired viscosity and N.V.M. content for this vehicle, even though there is a difference of 8°F in reaction temperature (See *Table C*).

Using the highest Norcross reading of Batch C and the lowest reading of Batch D, one finds a span of only two numbers with a difference of 8°F in the reaction temperature.

Consideration of these factors, in conjunction with the principle upon which the Norcross Viscosimeter functions, leads to the theory: the larger the diameter of the piston, the higher the readings of the Norcross Viscosimeter, and the more sensitivity to temperature fluctuations and a wider span necessary to meet a given viscosity range; conversely, the smaller the diameter of the piston, the lower the readings, the less sensitivity to temperature fluctuations, a narrower span to meet a given viscosity range. To ascertain the optimum points for any or all types of alkyds or varnishes is beyond the scope of this project. Final Norcross readings between 30 and 70 will give satisfactory results for most alkyds.

When heat bodying linseed oil the graphs show much more variation than with the alkyd varnishes. There is very little difference in viscosity between raw and polymerized linseed oil when taken at 560°F. The Norcross instrument requires a larger piston, so that the recorder will show end point viscosities reading

between 20 and 40.

This increases the sensitivity to a point where thixotropy, temperature fluxations, skins, entrapped inert gas or steam bubbles, and variations in the same oil, affects the readings of the Norcross from batch to batch to such an extent it may not be too accurate for end point of polymerization. However, it has been noted that the higher the viscosity specification of heat polymerized linseed oil, the better the opportunity for the Norcross Viscosimeter to meet these viscosity limits of the specification.

Some of these variation causes are assumed to be a build-up of skins on the piston rod to prevent free flow of oil, and also slightly affect the weight of the piston — or perhaps the piston did not go down far enough into the well to cause the cam and timing device to give the correct timing results.

Figure 9, Batch A is aged refined linseed oil, and Batch B is catalyzed linseed oil bodyed at 580°F. Batch B did not fall within the specified square outlining the end point viscosity tolerance.

The operators of the reactors will

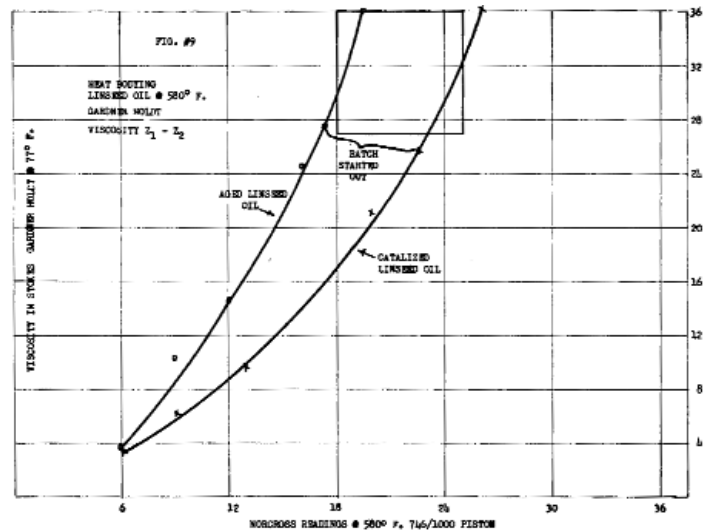


Figure 9

probably have to clean more often and have much more experience to determine end point viscosity specifications when heat polymerizing oil.

Conclusion

Considering all factors concerned, the committee feels that a considerable amount of progress has been made to obtain instrumentation for the continuous recording of viscosity in large closed reactors at processing temperature. Although each of the instruments mentioned in this report were designed for viscosity determination, they were not readily adaptable to our purpose.

Observations which have been made indicate that instruments can be designed by the various manufacturers for measurement of polymerization in heavy industrial equipment.

This type of instrumentation is not expected to entirely replace the normally conducted tests to determine end point of polymerization, but it will give the operators a continuous record of the state of the polymer size. Operators with a backlog of

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experience have been able to determine end point of polymerization with the timed falling plummet type of instrument, such as the Norcross Viscosimeter.

Small temperature changes and inert gas bubbles do not seem to greatly affect the instrument's recording and with this advantage, as well as an extensive range and excellent sensitivity, satisfactory results should be obtained. The usual normal cleaning of the reactor with caustic will clean the instrument at the same time, sufficiently well to keep it operating smoothly.

For the manufacture of heat bodied oils, and polymers of similar nature and also alkyd resins with more than 60% oil acids, the sensitivity of the instruments must be raised to a point where gels, temperature change, etc., often cause continuous recording results to be erratic from batch to batch of the same material.

Attempts were made to include all available types of devices designed to indicate viscosity in large resin reactor equipment, but it is quite possible that some manufacturers making instruments for this purpose were unknown to the committee. It is hoped that in such a situation the manufacturer will forward information on the instrument to the Chicago Club. The results of the use of the instrument would be published as an appendix to this report at some future date.

We wish to express our appreciation for the cooperation of manufacturers who have made available instruments and facilities for our studies:
 Brookfield Engineering Laboratories,
 General Electric Co., Fisher-Porter Co.,

Norcross Corp., Armstrong Paint & Varnish Works, Stresen-Reuter, Inc., Sherwin-Williams Co.

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- (1) January, 1950, *Chemical Engineering*, A.W. Shaw, Engineer, Worthington Pump and Machinery Corp.
- (2) Brookfield Engineering Laboratories, Porter Street, Stoughton, MA.
- (3) General Electric Co.
- (4) Fisher-Porter Co., Hatboro, PA.
- (5) Norcross Corp., Newton, MA.
- (6) The Rich-Roth Co., 673 Connecticut Blvd., East Hartford, CT.
- (7) Baldwin-Lima-Hamilton Corp. (Strain Gauges), Philadelphia, PA.
- (8) Sanborn Co. (Strain Gauge Recorder), Cambridge, MA.

Diagram of Automatically Measuring Viscosity with Ultra-Viscoson

Fig. #10

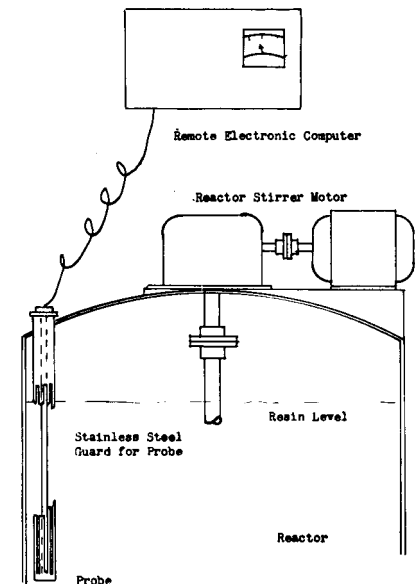


Figure 10

Diagram of Strain Mounting on Large Resin Reactors for Continuous Viscosity Recording

Fig. #11

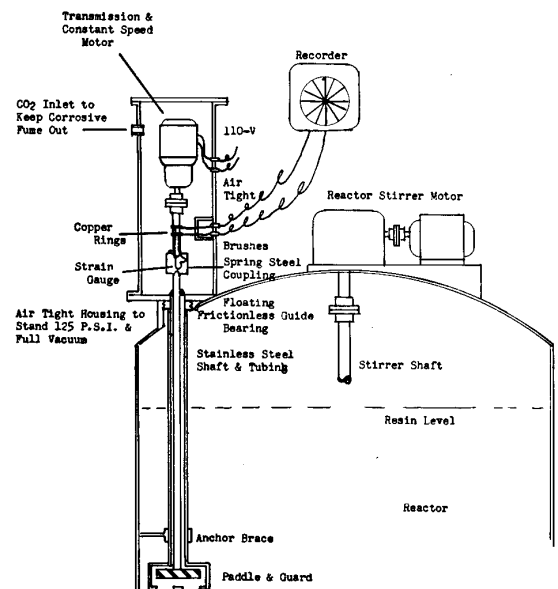


Figure 11