

## The Design and Application of an Automatic Endless-Belt Polymer Fractionator

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### Synopsis

The automatic endless belt polymer fractionator utilizes a continuous application and multistage extraction technique. A thin coating of polymer deposited on a slowly moving endless belt which passes through a series of solvent-nonsolvent mixtures of increasing solvent strength is fractionally dissolved. Discussion includes the description of the construction of the apparatus, details and results of fractionations of Neoprene W and polytetramethylene ether glycol, fractionation techniques and subsequent work-up of the fractions, "large scale" preparative fractionations, and general performance characteristics.

### INTRODUCTION

For a number of years, many different techniques have been used to fractionate polymers. These techniques have generally been divided into two categories: those, such as ultracentrifugation, in which no actual isolation of fractions takes place, and those in which fractions are actually isolated and characterized. Extraction and precipitation techniques are generally used in the latter. Recently, a great deal has been published on the relatively new technique of gel permeation chromatography, which can give fractionation data with or without actual isolation of the fractions. Recent textbooks on polymer characterization give good presentations of the field of fractionation as well as extensive bibliographies on the subject.<sup>1</sup>

Because of some difficulties encountered with certain elastomeric materials in applying existing techniques to the fractionation and subsequent isolation of fractions for further characterization, a better fractionation system was sought by our laboratory. The simplest and most successful technique then in use in our laboratories was that of the batchwise extraction and isolation of fractions from an elastomer sample coated on a small piece of cloth. While successful, the technique was time consuming, inefficient, and yielded only a few fractions representing a very small amount of material.

In an attempt to improve this same fractionation approach, an instrument was designed and built which accomplished the goal of a more automatic, rapid, and efficient fractionation system that could fractionate larger quantities of elastomers into more fractions than the previous technique.

This instrument was labeled the automatic endless-belt polymer fractionator.<sup>2</sup>

## EXPERIMENTAL

### Principle of Operation

Polymer fractionation using the endless belt fractionator is based upon a dissolution technique for separation. The basic design of the apparatus is shown in Figure 1. A polymer is dissolved in a suitable solvent and placed in a reservoir. Gravity feeds the polymer solution to the coating heads which apply a thin coating of the solution to both sides of the slowly moving belt. A drying region evaporates the solvent, and the thin film of polymer adhering to the belt is extracted in a continuous fashion in a series of tubes containing solvent-*n*-solvent mixtures held at a constant temperature.

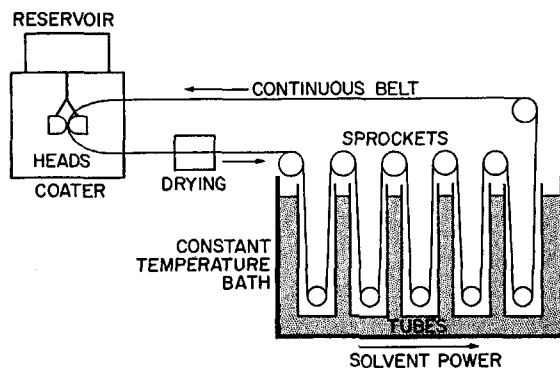


Fig. 1. Diagram of the basic constituents of the continuous-belt polymer fractionator.

The solutions are so chosen that the tube nearest the application area contains the poorest solvent for the polymer, and thus only the most soluble material will be extracted from the polymer film, this normally being the lowest molecular weight material. The successive tubes contain liquid of increasing solvent strength, the last containing the best solvent, which assures that the belt is free of polymer as it leaves the fractionation area.

When the desired amount of material has been applied to the belt, the polymer solution flow is shut off and the belt is run until the last of the applied polymer has passed through the series of tubes. Then the individual fractions are aspirated out of the tubes into separate flasks, and the polymer is recovered by evaporating the solvent.

### Construction of Fractionator

The endless-belt polymer fractionator is shown in Figure 2, and its construction can be identified from this figure as follows: The stainless-steel

polymer solution reservoir is located in the upper left-hand corner of the figure, just above the polymer application area. A dipstick is located in the top, which serves to provide a means of monitoring the quantity of remaining polymer solution and an opening for the addition of polymer solution. A valve in the back of the reservoir splits the stream so that polymer solution is continuously applied to both sides of the belt as it passes slowly through the applicator area. This is done by means of gravity feed of the solution through thin horizontal slots in the applicator heads, the thickness applied being controlled by both the viscosity of the polymer solution and the angle of the heads contacting the belt. This angle is controlled by the knob on the left of the applicator.

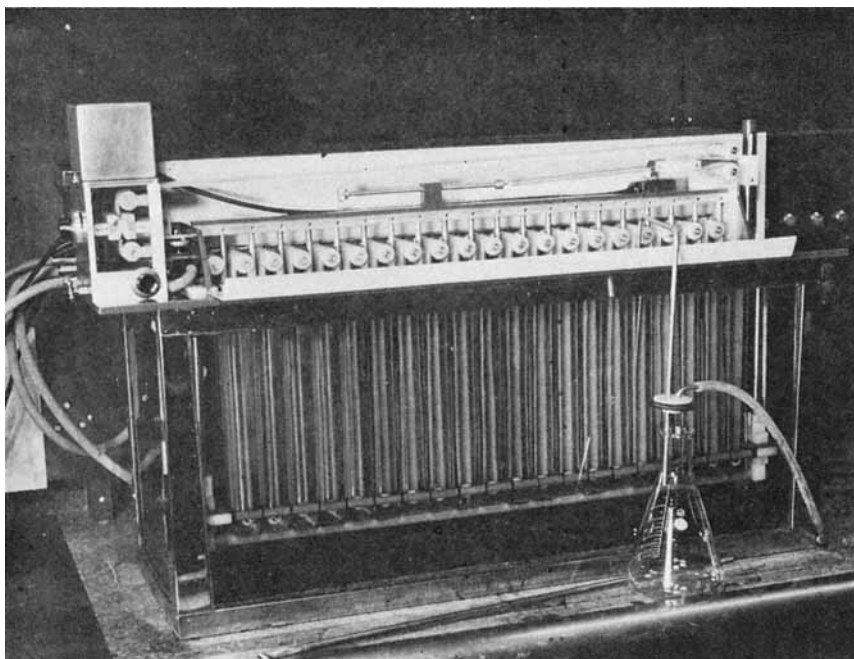


Fig. 2. Photograph of the continuous-belt polymer fractionator.

The belt is a 70-mm uncoated Cronar polyester film base (Du Pont) with normal sprocket perforations down both edges. The belt is approximately 50 ft long and is made into a loop by ultrasonic bonding of the two ends. With the exception of the sprocket hole edges, both sides of the belt are sandblasted for better polymer adherence. The applicator heads apply polymer only to the sandblasted portion of the belt.

The wet polymer film on the belt is continuously dried as it passes through nitrogen jets directed at both the top and bottom of the belt and located to the immediate right of the applicator housing in the figure. The speed of the belt can be varied from 0 to 36 in./min by the knob at the

front base of the applicator housing which controls a variable speed transmission to the belt drive.

Fractionation takes place in the 20 rectangular glass tubes containing various solvent mixtures. These tubes are suspended in a constant temperature bath by means of the frame shown. Access to the upper part of the tubes is by means of a hinged cover, shown open in the center of the figure. Drive sprockets located at the top of the tubes and others suspended from rods into the bottoms provide a path for the belt which loops to the bottom of each tube. The polymer deposited on the belt makes no contact with any mechanical parts.

Sitring of the solutions within the tubes is accomplished by a side-to-side oscillation of the bottom frame holding the tubes, while the tops of the tubes are held more firmly. The belt acts as a semirigid paddle in each tube, and the resistance causes an excellent stirring action in all tubes simultaneously, thus preventing the need for external stirring mechanisms.

Tension on the belt is maintained by an adjustable spring fastened to a floating sprocket, as shown in the upper right of the figure. A tab fastened to the floating sprocket and positioned between two microswitches turns off the instrument in case of belt failure.

The drive motor which drives a stainless steel chain that turns the sprockets is located behind the upper sprocket compartment shown. The constant-temperature control equipment is located in this same compartment, which has an air purge to prevent an accidental vapor buildup in this area.

A control box which is separate from the fractionator controls the motors, heaters, etc., of the fractionator and is equipped with a timer to shut off the instrument when operating over the weekend.

A tank immersed in the bath is located behind the tubes and is attached to the bottom of the chassis that rests on the 30-gallon aquarium. Various solvent-nonsolvent liquids can be placed in the tank, and nitrogen is then saturated by sparging it through the solvent mixture. The saturated nitrogen can then be bled into the area immediately above the tubes, providing an inert atmosphere which causes a minimum of evaporation of the fractionation solvents.

The sprockets in the apparatus are made of nylon and are mounted using stainless steel shafts and rods. The glass tubes were specially blown for the instrument and have dimensions of  $12 \times 4 \times 1\frac{1}{4}$  in., each holding 600 ml of solvent. The dimensions of the fractionator are approximately 23 in. high, 40 in. wide, and 15 in. deep.

The apparatus for aspirating the solution from the tubes at the conclusion of the fractionation is shown in front of the fractionator in Figure 2. It consists of a diptube with a plastic tip which runs through the cap shown into a flask. A vacuum line passes through the cap which has a hole in the top and a rubber disc which makes a seal with the flask. To operate, the diptube is placed at the bottom of a glass tube and the operator controls the aspiration rate with his finger using the hole in the cap.

The metal tube lying in a horizontal position in front of the fractionator is used to dry the tubes after emptying and consists of a series of holes which direct nitrogen into each tube.

### Fractionation Details

The fractionations of two quite different polymeric materials have been selected to demonstrate the capabilities of the apparatus. Both the Neoprene W elastomer and the polytetramethylene ether glycol (PTMEG) were plant samples and were fractionated without purification. Reagent-grade solvents were used in all fractionation work.

For the Neoprene W fractionation, methanol was placed in the first two tubes to extract the resin soap, stabilizers, and any other methanol-soluble additives. The solvent-nonsolvent fractionation mixtures were prepared by weighing the solvents into 1-liter Erlenmeyer flasks and utilizing the densities of the benzene solvent and the isopropanol nonsolvent to calculate volume per cent.

The Neoprene W was cut into small pieces and dissolved in reagent-grade benzene to give a 10 weight-volume per cent solution of a thick syrup consistency. Ten milligrams of Neozone D rubber antioxidant (Du Pont) was placed in each of the fractionation tubes. Polymer was applied for 11 hr with an additional 10 hr of running without application to allow the neoprene film on the belt to pass through all of the tubes completing the extraction. The belt ran at 1 in./min and the fractionation temperature was held at 30°C.

Following fractionation, the solutions were aspirated out of the fractionator tubes along with several solvent rinsings of the belt and top sprockets. The solutions were then taken to dryness under nitrogen jets in preweighed disposable aluminum pans placed on plates heated to approximately 50°C with circulating hot water. The pans were precleaned by rinsing with benzene and drying under nitrogen before weighing. The fractionating solvents were evaporated in a hood in approximately 2 hr, and the weight of polymer residue in the pans was obtained by reweighing.

Inherent viscosities were obtained on all fractions at 30°C by dissolving 0.1 g of polymer fraction in 100 ml of benzene. The fractions were dissolved in disposable bottles with moderate shaking. Viscosities were then run by first placing extraction thimbles in the bottles to filter any dust or gel particles and then pipetting 10 ml of the filtered solution into Cannon-Fenske size 75 viscometers.

The PTMEG sample was of a thin syrupy consistency and required no dilution. Thirty milligrams of Ionol antioxidant stabilizer (Shell Chemical Co.) was placed in each fractionation tube. As in the case of Neoprene W, polymer was coated on the continuous belt for 11 hr. However, only 5 hr were required to remove the applied polymer since the belt speed was 2 in./min. The fractionation was run at 50°C, isopropanol being used as the solvent while distilled water was used as the nonsolvent.

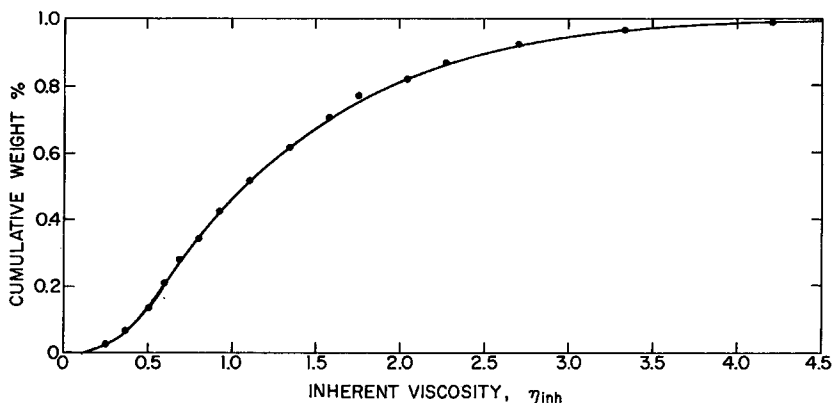


Fig. 3. Integral viscosity distribution for Neoprene W.

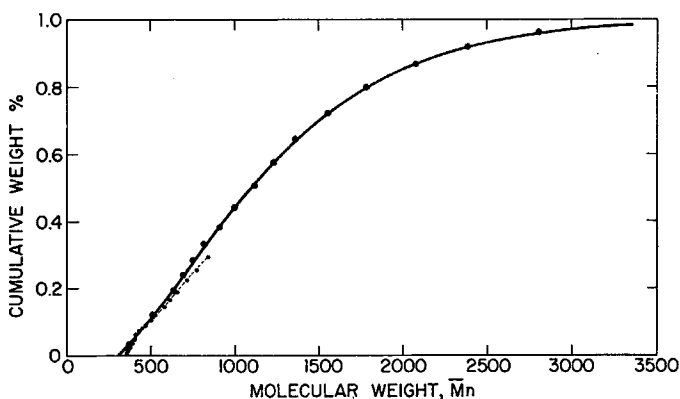


Fig. 4. Integral molecular weight distributions for two different lots of PTME glycol: (—●—) data from continuous belt fractionator; (—○—) data from Conley and Kubitz molecular distillation fractionation.<sup>4</sup>

Following fractionation, the fractions were taken to dryness at 50°C under a stream of nitrogen. Forty-eight hr were required to achieve dryness as determined by no further weight loss.

The hydroxyl numbers were determined by acetylating with acetic anhydride-pyridine solution, hydrolyzing the excess reagent with water, and titrating with standard sodium hydroxide solution.

## RESULTS AND DISCUSSION

The fractionation curves for Neoprene W and PTMEG are shown in Figures 3 and 4. The integral curve that results from plotting the cumulative wt-% versus molecular weight or solution viscosity is shown. The cumulative wt-% is obtained using the method of Schulz and Dinglinger,<sup>3</sup> in which a given fraction is plotted at the cumulative wt-% of the previous fractions plus one half the wt-% of the given fraction. The fractionation data for the two polymers are shown in Tables I and II.

TABLE I  
 Neoprene W Fractionation

Fraction	Weight, g	% <sup>a</sup>	$\eta_{inh}^{30^\circ}$	Solvent, vol-%
1	0.1361	4.58	soap	methanol
2	0.0113	0.38	soap	methanol
3	0.1266	4.49	0.25	72.0
4	0.1380	4.89	0.37	74.0
5	0.2203	7.81	0.51	75.5
6	0.2067	7.32	0.60	76.0
7	0.1743	6.18	0.69	76.5
8	0.2141	7.59	0.81	77.0
9	0.2397	8.49	0.95	77.5
10	0.2724	9.65	1.11	78.0
11	0.2929	10.38	1.35	78.4
12	0.2206	7.82	1.59	78.6
13	0.1428	5.06	1.76	78.8
14	0.1333	4.72	2.05	79.0
15	0.1518	5.38	2.28	79.2
16	0.1393	4.94	2.71	79.4
17	0.0915	3.24	3.34	79.6
18	0.0499	1.77	4.21	80.0
19	0.0044	0.16	—	100
20	0.0032	0.11	—	100
	2.9692	100.00	1.31	
Whole			1.24	
			1.31	(when corrected for soap content)

<sup>a</sup> The per cents for fractions 1 and 2 are based on the total sample weight fractionated, while the per cents for fractions 3-20 are based on a sample weight which excludes fraction 1 and 2.

The results of the two fractionations shown are fairly typical of the capabilities of the belt fractionator based on the results of hundreds of fractionations involving dozens of different types of polymers. The distribution curves of the two materials as shown in Figures 3 and 4 are in agreement with fractionations of these polymers run by using other techniques.

Figure 4 shows a comparison of the integral molecular weight distribution of the PTMEG sample of  $\bar{M}_n = 920$  obtained using the belt fractionator with a sample of  $\bar{M}_n = 1000$  fractionated by Conley and Kubitz<sup>4</sup> using molecular distillation and endgroup analysis to determine molecular weight.

Good agreement is found for the low molecular weight fractions obtained by both methods. The increasing divergence of the data as  $\bar{M}_n$  increases can be attributed to the slightly higher average molecular weight of the polymer fractionated by distillation and the increasing difficulty of removing fractions by distillation as the molecular weight increases.

It should be noted that over 15 times more PTMEG was fractionated than Neoprene W in the same length of time. This is due primarily to the

TABLE II  
 PTME Glycol Fractionation

Fraction	Weight, g	%	$\bar{M}_n$	Solvent, vol-%
1	3.359	6.77	375	0
2	1.913	3.86	442	5
3	1.598	3.22	512	15
4	1.473	2.97	558	20
5	2.334	4.70	634	24
6	2.151	4.33	693	26
7	2.205	4.44	753	28
8	2.569	5.18	825	30
9	2.695	5.43	912	32
10	2.972	5.99	1002	34
11	3.440	6.93	1122	36
12	3.549	7.15	1232	38
13	3.672	7.40	1368	40
14	3.815	7.69	1558	42
15	3.845	7.75	1781	44
16	3.105	6.26	2078	46
17	2.258	4.55	2387	48
18	1.800	3.63	2805	50
19	0.613	1.24	—	70
20	0.254	0.51	—	100
	49.620	100.0	913	
Whole			920	

lower molecular weight of the PTMEG. Before calculation, all fraction weights were corrected for the known added stabilizer.

As standard procedure, a check on the fractionation of both polymers was made by comparing the viscosity or molecular weight of the whole polymers with the summation of the fractions. In the case of Neoprene W, the summation of the product of weight fraction times viscosity gave a value for inherent viscosity of 1.31, as compared to an inherent viscosity of 1.31 for the unfractionated material after a calculated correction for the soap found in tubes 1 and 2 was made on the original value of inherent viscosity 1.24. This resin soap effectively dilutes the whole polymer with respect to viscosity and is removed in the first two tubes of the fractionator, and therefore does not enter into the viscosity summation. The PTMEG has a number-average molecular weight of about 920, and by summing the product of the mole fraction of polymer in each fraction times the number-average molecular weight, a value of 913 was obtained.

A number of checks were made from time to time on the amount of polymer recovered in the fractions compared to the weight of polymer fractionated. Within experimental accuracy, total recovery has generally been observed. Since the last tube contains solvent of at least the dissolution power of the solvent that the polymer is dissolved in, the polymer will dissolve off the belt unless crosslinking or degradation occurs. These effects



can be minimized by sheltering from light and by use of a nitrogen atmosphere above the fractionating tubes.

Like other techniques such as precipitation and column extraction, the belt fractionator fractionates on a basis of solubility and not just molecular weight. This apparent shortcoming has been used to some advantage in fractionating copolymers to obtain fractions for compositional analysis. Solvents, temperatures, etc., can be chosen to optimize either molecular weight or compositional separation.

A very favorable condition exists in the belt fractionator for efficient extraction of material deposited on the belt. Looking at Neoprene W, for example, a 3-g sample that has been coated for 11 hr on the belt traveling 1 in./min would have sample applied 2.5 mil thick over the surface area of 2640 sq. in., and all portions of the coated polymer film would be exposed to agitated extracting solvent for 10 hr. On the average, 0.15 g of Neoprene W would be dissolved in each tube containing approximately 600 ml of extracting solvent. A theoretical calculation by Frensdorff<sup>5</sup> indicates that a  $\bar{M}_w/\bar{M}_n$  of 1.06 or better is possible with the fractionator. In a planned publication, Hoeker<sup>6</sup> reports an average  $\bar{M}_w/\bar{M}_n$  of 1.07 for several fractions from the belt fractionation of poly(methyl methacrylate) with a polydispersity ratio for the whole polymer of 1.7.

One of the uses of the fractionator is to prepare relatively large quantities of fractions for further physical and chemical studies. These "large scale" preparative fractionations yield approximately ten times as much material in each fraction as the conventional procedure already described. This is accomplished with some sacrifice in the narrowness of the fractions.

A typical preparative fractionation usually involves ten fractions instead of 20, and these are obtained by placing the same solvent-nonsolvent mixture in pairs of adjacent tubes, effectively doubling the path length and the exposure time of the polymer to a given solvent mixture. The speed of the belt can then be doubled, and the amount of polymer applied to the belt in a given length of time is thus doubled. In order to increase the amount of polymer fractionated even further, the belt speed is again doubled, giving four times the usual application and amount fractionated. Large-scale runs are usually run continuously for days, which means continuous 24-hr application compared to the 10-hr application usually used when fractionating for the purpose of obtaining molecular weight distribution. This adds another factor of 2.4 to the amount normally fractionated. The resulting tenfold increase in the amount of polymer fractionated is shown by the data in Table III. Once each day, solutions are removed and fresh solvent-nonsolvent solutions are added sequentially to each tube without shutting down the apparatus. It should be noted that very little operator attention time is required to fractionate relatively large quantities of polymer.

The instrument is quite versatile. If only three or four fractions are desired, several adjacent tubes can be filled with the same solvent-nonsolvent mixture and the belt can be run at a much faster speed than normal.

TABLE III  
*Preparative Fractionations*

Polymer	Grams Fractionated	Number of fractions	Number of days	Approxi- mate manhours
Neoprene W	348	10	25	50
Nordel <sup>a</sup> hydrocarbon elastomer	96	10	6	12
Viton <sup>a</sup> fluoroelastomer	271	10	5	10
Methyl methacrylate	61	11	1.5	3
Phenol formaldehyde	1048	7	10	20

<sup>a</sup> Du Pont's registered trademark.

If only a small amount of a few fractions is needed, only a few of the tubes need be used. Sometimes a particular region of the molecular weight distribution curve is of interest and the solvent-nonsolvent compositions are then chosen to resolve this region more completely.

Chemical separations with the belt fractionator are also possible, as illustrated by an experiment in which a black water-base ink was resolved into its various colored dyes utilizing solubility differences between the dyes. This separation was possible because of the very thin coating used and by making use of a spectrum of solvent polarity going from a benzene-rich methanol-benzene mixture through pure methanol to a final tube of water.

Fractionations have been run at temperatures ranging from 25°C to 50°C. The waterproofing material used in the constant temperature bath prevented going much above 50°C. The effect of higher temperatures and some solvents sometimes result in the extraction of small amounts of residues from the "Cronar" belt. In most cases, coating the belt with a thin coating of polyethylene by immersion in a hot toluene solution of polyethylene and then drying prevents this extraction. A stainless steel belt has been used successfully to fractionate polymer and could be used at elevated temperatures.

## CONCLUSIONS

The endless-belt polymer fractionator appears to be a very useful instrument for obtaining relatively large quantities of polymer fractions through relatively simple and straightforward procedures. The method is basically governed by the same rules and limitations that apply to other dissolution techniques for fractionating polymers, but has certain distinct advantages over batch extraction or precipitation techniques because of its continuous application and simultaneous multiextraction principle.

Because of its endless belt design, very little attention is required to operate it, and fractionations yielding several grams or more can be obtained in a 24-hr period, thus making it valuable as a research tool whenever

further data on the fractions are needed. By slight modification of the operating techniques, fractionation yield can be boosted by a factor of 10 for preparative fractionations.

Because of the large surface area of the belt, the very thin film of polymer coated on the belt, and the relatively long exposure of polymer to each solvent-nonsolvent solution, quite good equilibration is observed in each tube. This has been verified by preliminary experimental evidence as well as by theoretical considerations. The effects of polymer carry-over from tube to tube as well as the effects of solvent-nonsolvent composition changes during a run have both been shown to have minimal effects on the fractionation.

Although the fractionator was originally designed for fractionating elastomeric materials, the unit has also been used to successfully run other types of polymers as well as certain chemical mixtures.

The author gratefully acknowledges the dedicated effort and skill exhibited by Elmer E. Tompkins in the construction of the instrument described in this paper. In addition, appreciation is given to H. Karl Frensdorff for his assistance, particularly with regard to theoretical considerations of the performance of the instrument.

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