GEL PERMEATION CHROMATOGRAPHY AND POLYMER ADDITIVE SYSTEMS

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SUMMARY

Chromatograms obtained on solvent extracts of polymer systems can be used to identify the vendor of the polymer in much the same manner as absorption spectra are used to identify the base polymer. The chromatogram in its entirety is compared to reference chromatograms obtained on similar extracts of known polymers from known vendors. The individual components can be identified by comparison of the individual peaks to chromatograms of known compounds. The same procedure can be used to follow depletion of additive components during environmental testing and/or field exposure by determining peak heights or peak areas. Quantitative determination of additives can be made by either or both of the above measurements. Chromatograms of the additive systems in several commercially available polymer compounds are shown along with quantitative calibrative curves for various additive components. Chromatograms illustrating the effects of processing and environmental conditioning on additive concentrations are also presented.

INTRODUCTION

Since its introduction by MOORE[1] gel permeation chromatography (GPC) has become a "laboratory word" in those laboratories engaged in the analysis and characterization of polymeric compounds. One normally associates GPC with the determination of molecular weight distributions (MWD), however the technique has been used successfully to separate the components of complex mixtures for subsequent identification by other means. BARTOSIEWICZ[2] has used it in the analysis of coating systems, LARSON[3] used it for the analysis of epoxides and SPELL[4] used GPC and infrared spectrophotometry in the separation and identification of the components in complex organic mixtures.

This paper illustrates how the chromatograms obtained on extracted polymer additive systems can be used in the identification of the commercial supplier of the polymer compound as well as in the identification of the individual components of the additive system. Chromatograms obtained in the same manner can be used in the evaluation of antioxidant and plasticizer systems during processing and/or environmental exposure. The chromatogram in its entirety is used, much like absorption spectra, to identify an additive system indicative of a particular supplier. The elution

volumes or count numbers of the individual peaks are used to identify the components and the peak area and/or height is used in determining the concentration of the components.

The additive system incorporated into a polymer should be carefully selected to give the best performance in the environment to which the finished product will eventually be exposed. This means that the supplier of polymeric compounds might use the same base resin for various end uses, changing only the additive system in order to meet specific requirements. It also means that the manufacturer of formed plastic parts probably inventories several types of polymer, differing only in the additive system. Screening a polymer-additive formulation for a specific end use can take up to a years' testing under environmental conditions. It is necessary, therefore, to insure that the parts being tested do contain the proper additive system and that the effects of the exposure on the system can be meaningfully monitored.

The normal procedure for monitoring such a system, if it can indeed be monitored, is to extract the additives from the sample and measure the concentration of the extracted components by appropriate instrumental techniques. This procedure is not only time consuming but in many cases just does not do the job. Additive systems can, and do, contain several components which cannot be individually determined or measured in such a procedure. The chromatographic procedure described herein allows one to analyze most additive systems in a rapid and straightforward manner.

EQUIPMENT

The equipment consists of a Waters Associates' Model 100 gel permeation chromatograph unit operated at room temperature (*ca.* 30°) using tetrahydrofuran (THF) at a flow rate of 2 cc/min. Nine 4-ft. stainless steel GPC columns packed with Poragel A-1 were used in the study. The columns were packed in this laboratory by filling with a THF–Poragel slurry (previously swollen in THF for a minimum of 24 h). The column to be packed was placed in an upright position, a vacuum applied to the lower end and the slurry slowly poured in the top. The column was constantly vibrated during the packing procedure. The nine columns in series have an interstitial volume of 100 ml (40 counts). The plate count for this system was calculated to be 460 using 1 % trichlorobenzene in THF and a 10-sec injection time. The molecular weight exclusion limit for Poragel A-1 is 1000.

EXPERIMENTAL

Reference chromatograms are obtained on additive systems of polymers received from known suppliers. For qualitative work the sample is cut into pea-size pieces, just covered with degassed solvent and allowed to stand overnight. For quantitative analyses the sample is preferably ground in a Wiley mill to pass a 20 mesh screen and 10 g of the powder is extracted with 20 ml of degassed THF overnight. Two milliliters of the extract is injected onto the columns. The sensitivity of the instrument is normally set at 2 ×.

Calibration curves (Fig. 1) for known compounds are made by plotting peak heights and/or peak areas, taken from chromatograms run on solutions of known
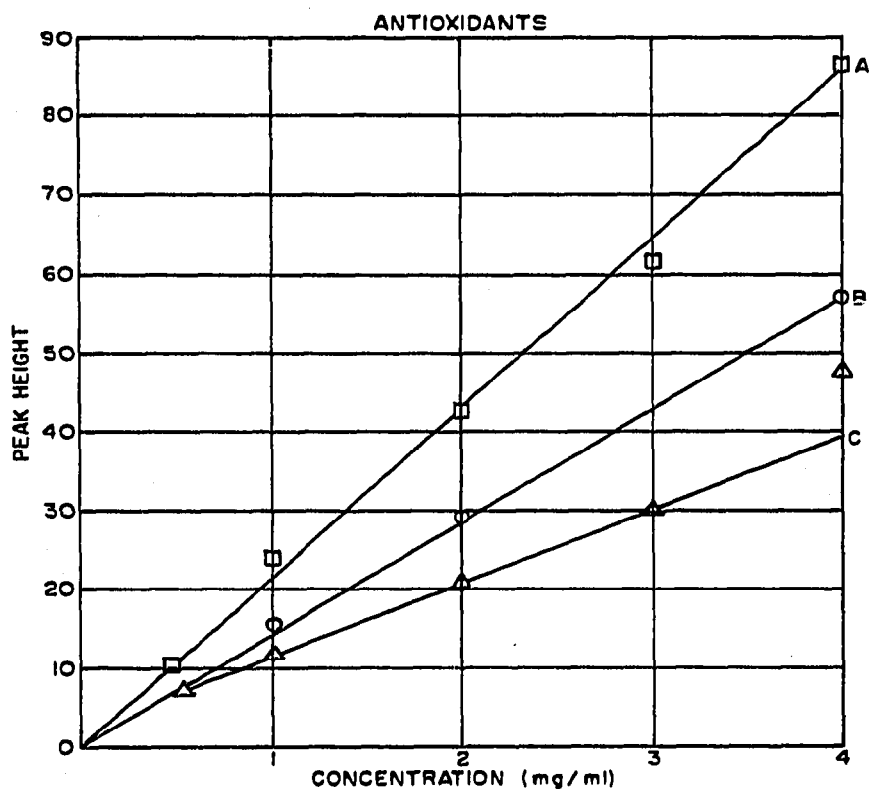
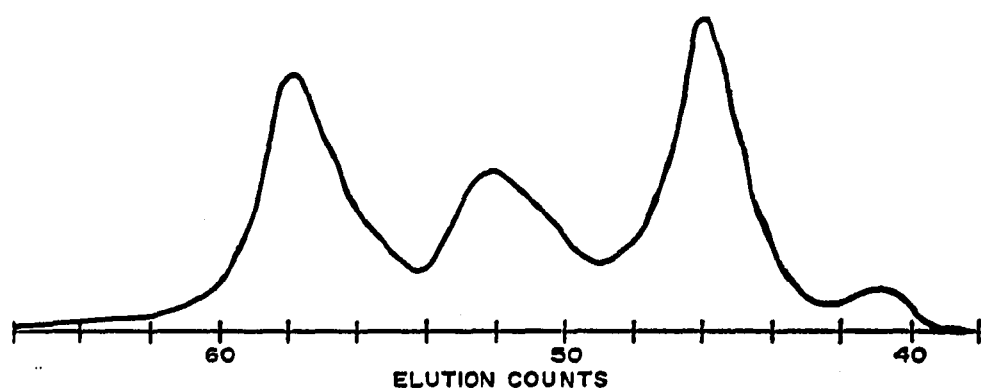Fig. 1. Antioxidant calibration curve.

Fig. 2. Chromatogram of polymer A extract.

concentrations, against the concentration. Correlation charts showing different additive components and their elution volumes, or counts, can be made to facilitate the identification of additives in unknown polymers. Such charts are valid only for a specific set of columns and must be used with discretion.

Identification of suppliers

Figs. 2–5 show chromatograms obtained on the THF extracted additive systems in four commercial polypropylenes. One can see from these chromatograms that there
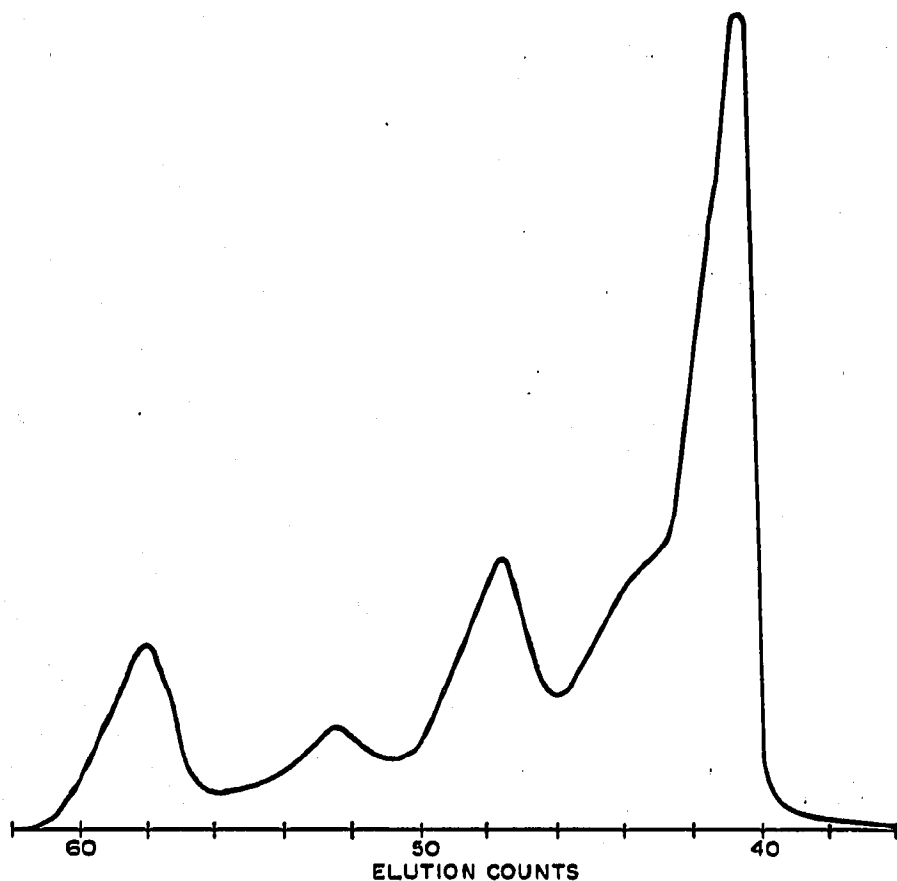
Fig. 3. Chromatogram of polymer B extract.
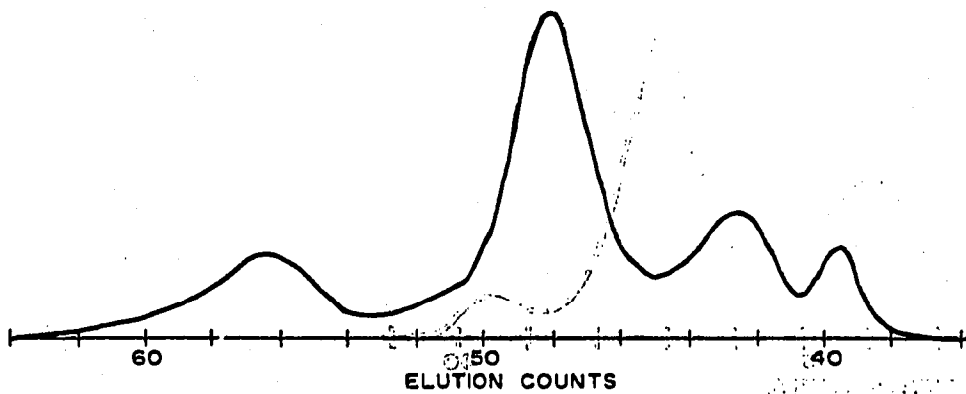
Fig. 4. Chromatogram of polymer C extract.
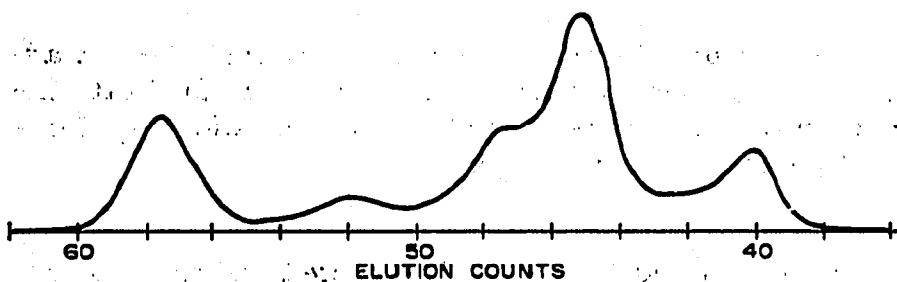
Fig. 5. Chromatogram of polymer D extract.

are significant differences in the additive systems which can be used as a basis for identification. Chromatograms such as these have been obtained on more than twenty commercially available polypropylenes and so far no two have had the same system. There is no rule of course saying that two or more suppliers cannot use an identical additive system. Should such a situation arise one would have to explore other techniques of identification before making a final decision. These other techniques might
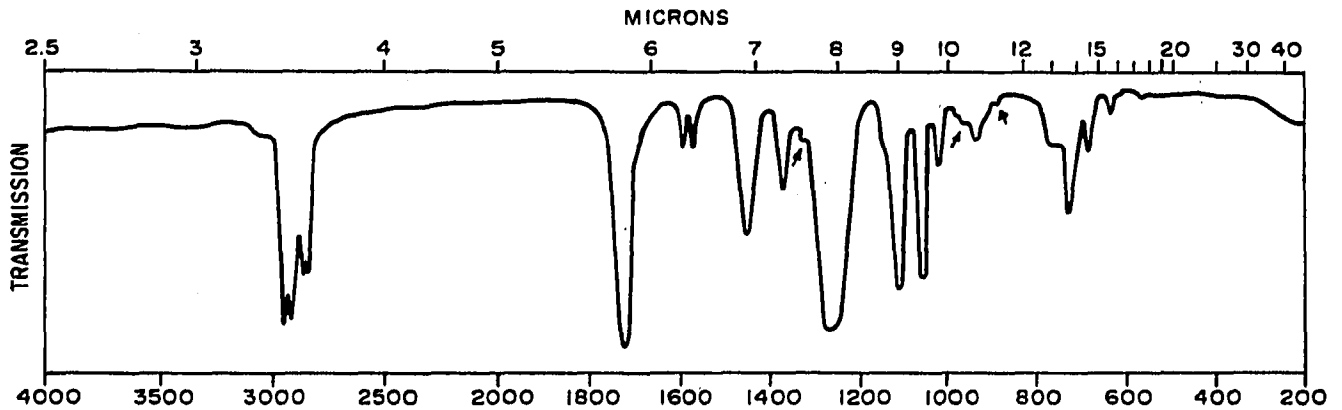
Fig. 6. PVC plasticizer system.
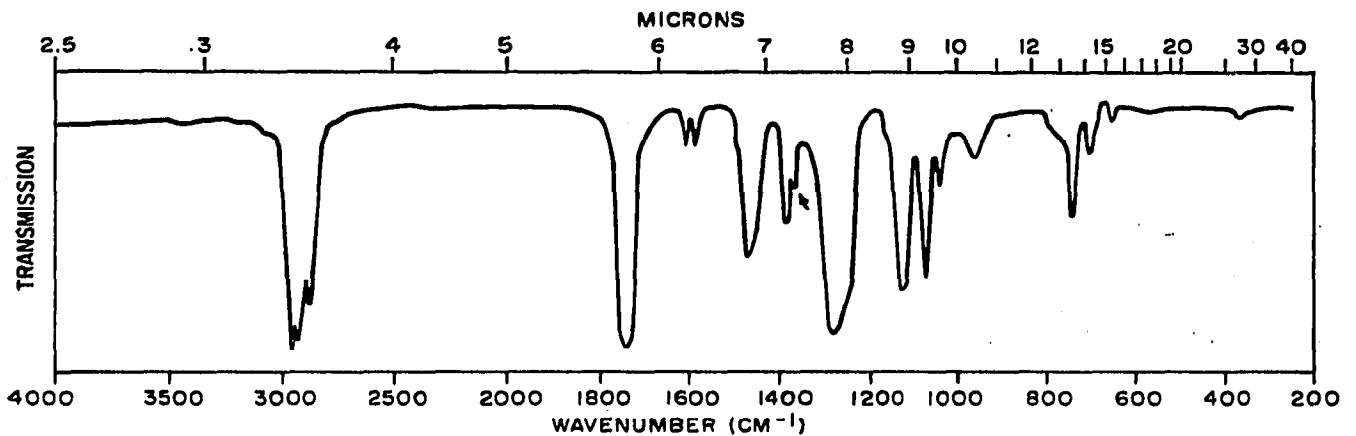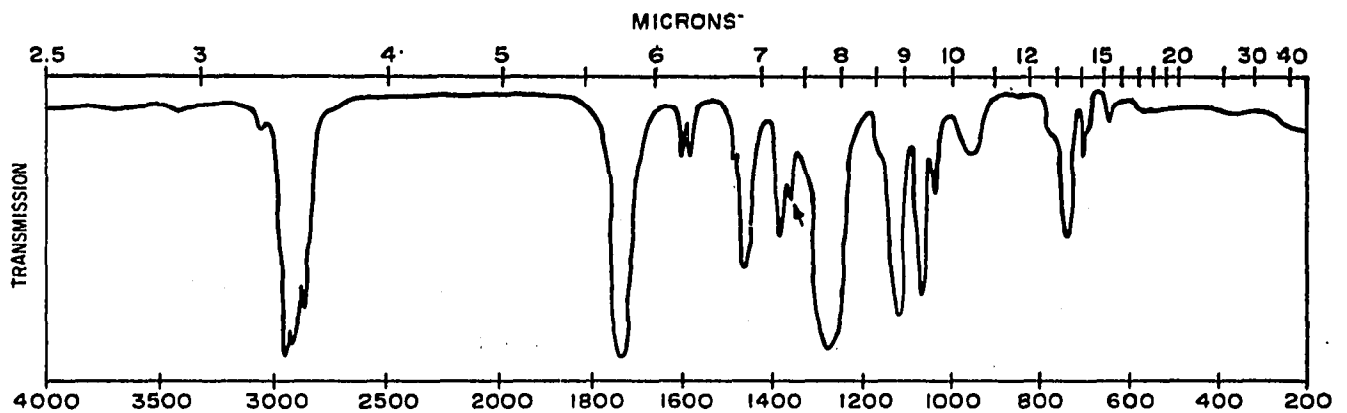
Fig. 7. PVC plasticizer system.

Fig. 8. PVC plasticizer system.

include analysis for catalyst residues, MWD etc. A thorough investigation of the
sample history would certainly be helpful. In any event the chromatogram would have
narrowed the search to two or three possibilities.

Figs. 6–8 show the infrared (IR) spectra of plasticizer systems extracted from
poly(vinyl chloride) compounds supplied by different vendors. There are differences
in these spectra (indicated by arrows) which might be used in distinguishing between
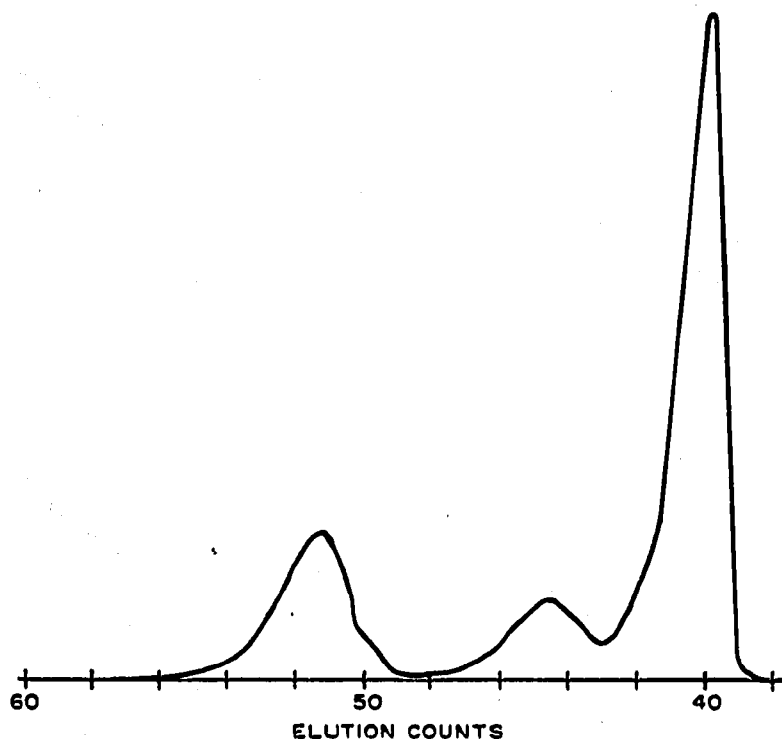them, however, after exposure to field environment these differences are often masked
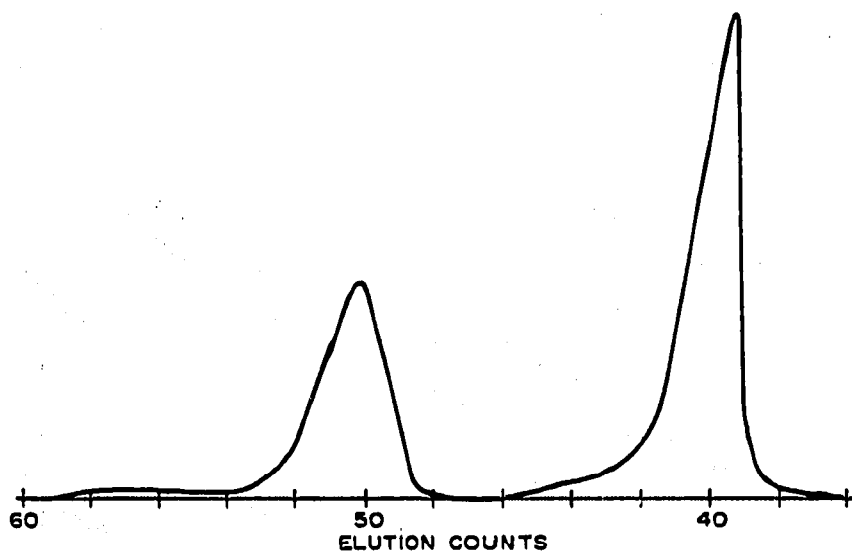
Fig. 9. Plasticizer from supplier A.

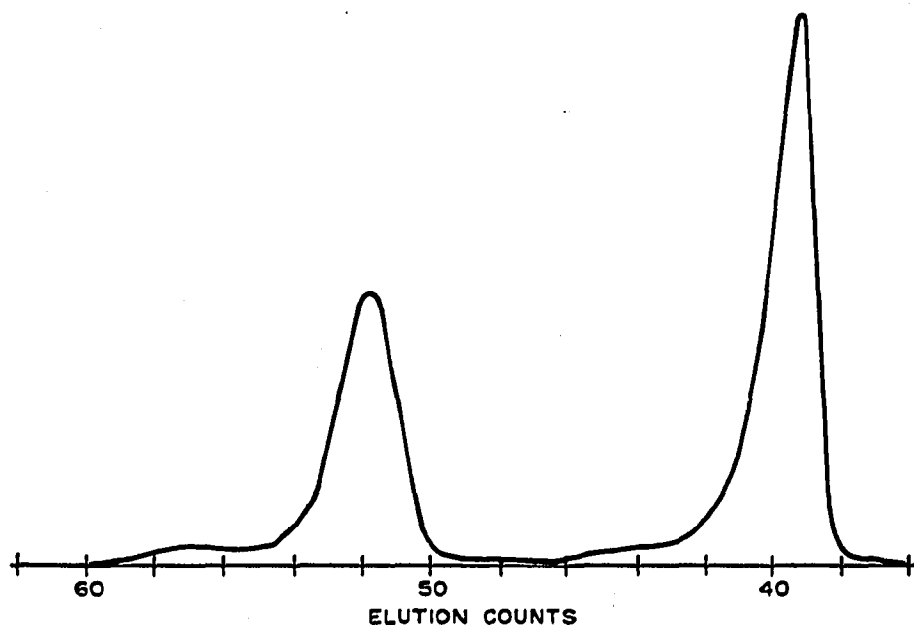Fig. 10. Plasticizer from supplier B.

ELUTION COUNTS

Fig. 11. Plasticizer from supplier C.

by contaminants or have actually vanished. Figs. 9, 10 and 11 show the chromatograms of these same three systems. It is quite obvious from these figures that there are indeed very significant differences in the compounds. The peak at 40 counts is PVC resin; the other peaks are plasticizer components. The IR spectra indicated the plasticizers to be phthalic acid derivatives, but it would be difficult to detect the second component in Fig. 9 (ca. 44 counts). IR analyses of GPC fractions show the phthalate in Figs. 9 and 10 to be di-isodecyl phthalate (50.3 counts) and in Fig. 11 to be di-octyl phthalate (52.3 counts). The second component in Fig. 9 is an epoxy derivative.
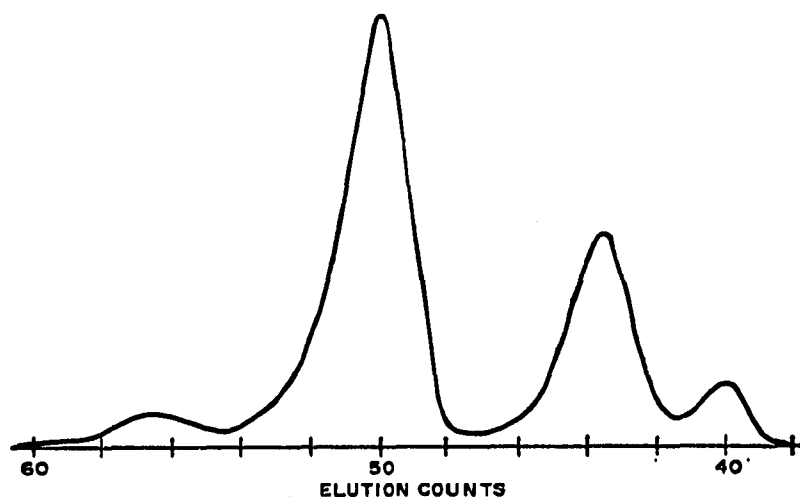

ELUTION COUNTS

Fig. 12. PVC plasticizer system before exposure.

The procedure followed in our laboratory now for the identification of such plasticizer systems would be to determine by IR analysis that a phthalate system is present. A chromatogram would then be obtained on the extract and the identity of the specific phthalate would be determined by its elution count. The GPC fractions would be collected for subsequent positive identification by IR.

Environmental effects

Figs. 12–14 show one of the plasticizer systems previously discussed after various periods of environmental exposure. Perhaps the most interesting point here is not the decreasing phthalate peak (50.3 counts) but the increasing epoxy derivative peak at 43.5 counts. Calculations have shown that the increase in epoxy content of the sample cannot be attributed to the increase in PVC resin required to offset the phthalate ester loss. It is assumed from this information that the epoxy derivative is migrating to the phthalate-poor areas during exposure. Information such as this is invaluable in helping to choose the most satisfactory materials and designs for functional parts in consumer destined products.

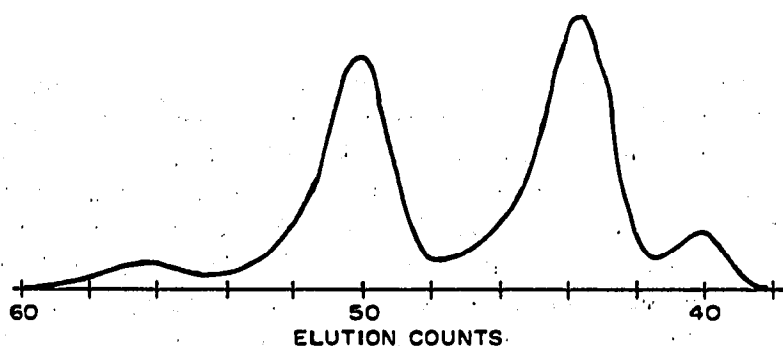Other additive systems can be followed in the same manner.

ELUTION COUNTS

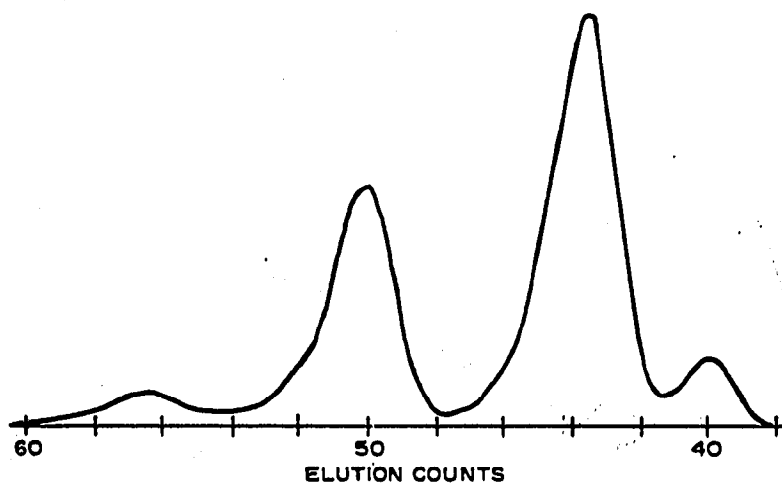Fig. 13. PVC plasticizer system after short exposure.

ELUTION COUNTS

Fig. 14. PVC plasticizer system after long exposure.

Effects of processing

Figs. 15–17 show the effects of processing on a four component stabilizer system. Fig. 15 shows the chromatogram of the virgin material. The peaks are labeled as A, B, C and D. Fig. 16 shows the chromatogram of the same system after a short exposure to processing conditions. Peak "B" is diminishing whereas peaks A, C and D remain unchanged. In Fig. 17, peak "B" has almost completely disappeared while peaks A, C and D still remain unchanged. If the purpose of component "B" is to
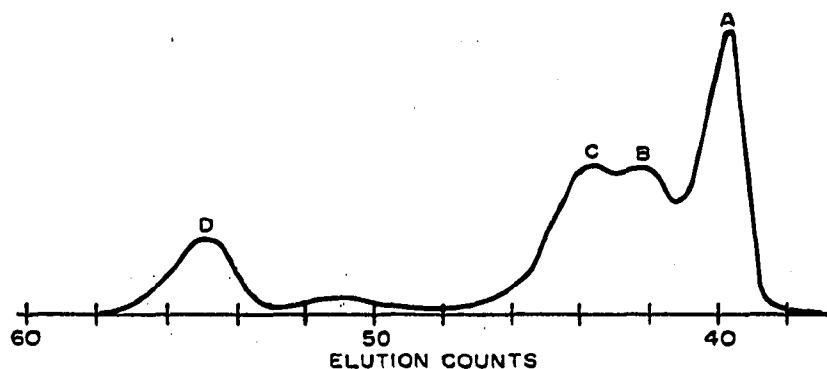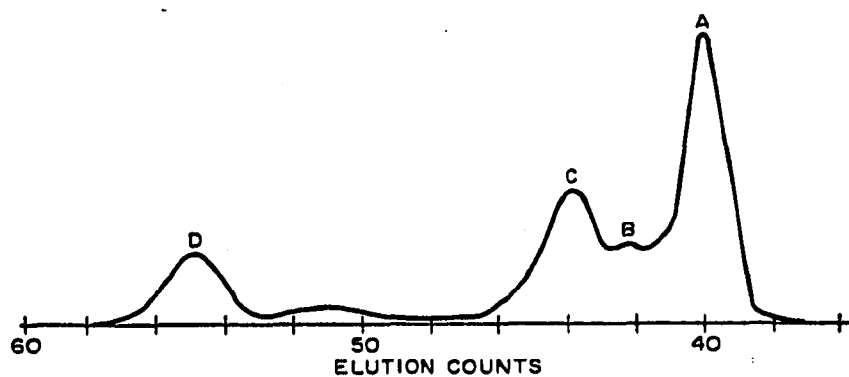
Fig. 15. Stabilizer system before processing.
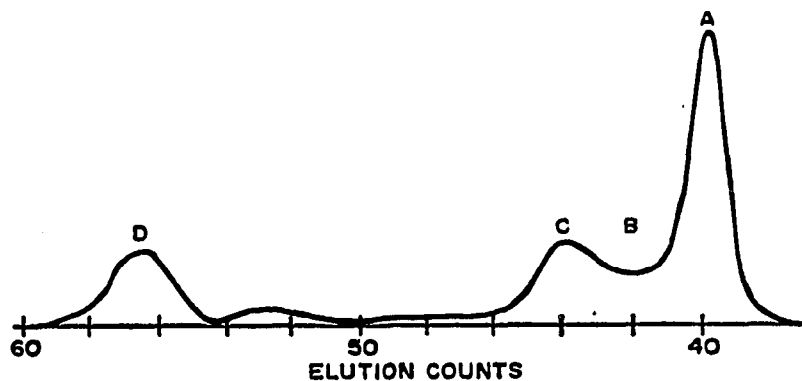
Fig. 16. Stabilizer system during processing.

Fig. 17. Stabilizer system after processing.

protect the material during processing then it is apparently doing its job. On the other hand if it is added to give long-term protection⟧then its use needs to be re-evaluated and a more permanent substitute found.

CONCLUSION

The use of a low porosity packing material (Poragel A-1) in GPC columns enables one to distinguish between various commercial polymers by characterizing the additive systems. The chromatograms in their entirety can be used to identify the supplier and the individual peaks can be used to identify the additive components. Chromatograms of additive systems obtained on samples from field use and processing areas can be used for evaluation of additive systems designed for specific applications.

REFERENCES

1 J. D. MOORE, *J. Polym. Sci.*, 2 (1964) 835.
2 R. L. BARTOSIEWICZ, *4th Intern. Seminar Gel Permeation Chromatography, Miami Beach, 1967.*
3 F. N. LARSON, *6th Intern. Seminar Gel Permeation Chromatography, Miami Beach, 1968.*
4 H. L. SPELL, *4th Intern. Seminar Gel Permeation Chromatography, Miami Beach, 1967.*