

CHROM. 14.893

Note

Determination of flow-improver additives in new and aged insulating oils by gel permeation chromatography

MICHEL DUVAL*, SERGE LAMOTHE, DANIEL CAUCHON, CLAUDE LAMARRE and YVES GIGUERE

Institut de Recherche d'Hydro-Québec, Varennes, Québec J0L 2P0 (Canada)

(Received March 11th, 1982)

Most power transformers are filled with mineral oil in order to provide electrical insulation and ensure dissipation of the heat generated in the windings¹. In northern climates such as Canada's, transformer oils must maintain good flow characteristics at very low temperatures. Naphthenic oils generally meet this requirement, although their availability in the future is uncertain, but the paraffinic oils proposed as alternatives by the oil industry tend to solidify, and flow-improving additives must be incorporated to lower their pour-point temperature.

Such additives are mostly polymers of the aromatic or naphthalene type with long aliphatic side-chains to prevent the formation of large paraffinic crystals in the oil². Their analysis, increasingly important for electrical utilities to be able to control the quality of new and aged transformer oils, has been undertaken by gel permeation chromatography (GPC) in this work.

EXPERIMENTAL

A high-performance liquid chromatography system, equipped with a Model M6000 high-pressure liquid pump and a Model U6K injector from Waters Assoc., a Varichrom variable-wavelength ultraviolet detector from Varian, and a Fluoromonitor fluorescence detector from LDC, was used in the gel permeation mode.

The following combination of six μ -Styragel columns from Waters Assoc. was found to give optimum separation of the additives from the oils: three columns of 10 nm, one of 50 nm, one of 100 nm and one of 1000 nm pore size. Tetrahydrofuran solvent (Omni-solv grade) was filtered on 0.45- μ m Millipore filters prior to use. Typical injection volumes of oil were 100 μ l.

The samples of naphthenic oil (Voltesso 35), paraffinic oil (QS 2598 A), base oils (without additives) and corresponding flow-improvers (Paraflo 149 for Voltesso 35 and Flow Improver 77-268 for QS 2598A) were obtained from Imperial Oil (Canada).

Samples of oxidized oil were prepared according to ASTM method D2440 (25 g of oil, 110°C, oxygen, 1 l/h, 30 cm of copper wire) and samples of oil subjected to corona discharges according to a modified version of ASTM method D2300 (Pirelli test)³.

RESULTS AND DISCUSSION

Analysis of new oils

Typical chromatograms of transformer oils and flow-improvers, using the UV detector, are shown in Figs. 1 and 2. It can be seen that the flow-improvers are composed of two parts (Fig. 1A and 2A): a polymer part, which elutes first in the GPC mode, and an oily part, possibly incorporated by the manufacturer to facilitate handling. The same figures show that there is no interference between the polymer peak of the flow-improver and the main peak of transformer oil: at the position where the polymer peak elutes (arrow) there is no UV absorption due to the oil (broken line). UV detection at 230 nm corresponds to the optimum combination of sensitivity and separation of the polymer peak: the peak heights of both the polymer and the transformer oil increase rapidly from 350 to 200 nm but the resolution decreases below 230 nm.

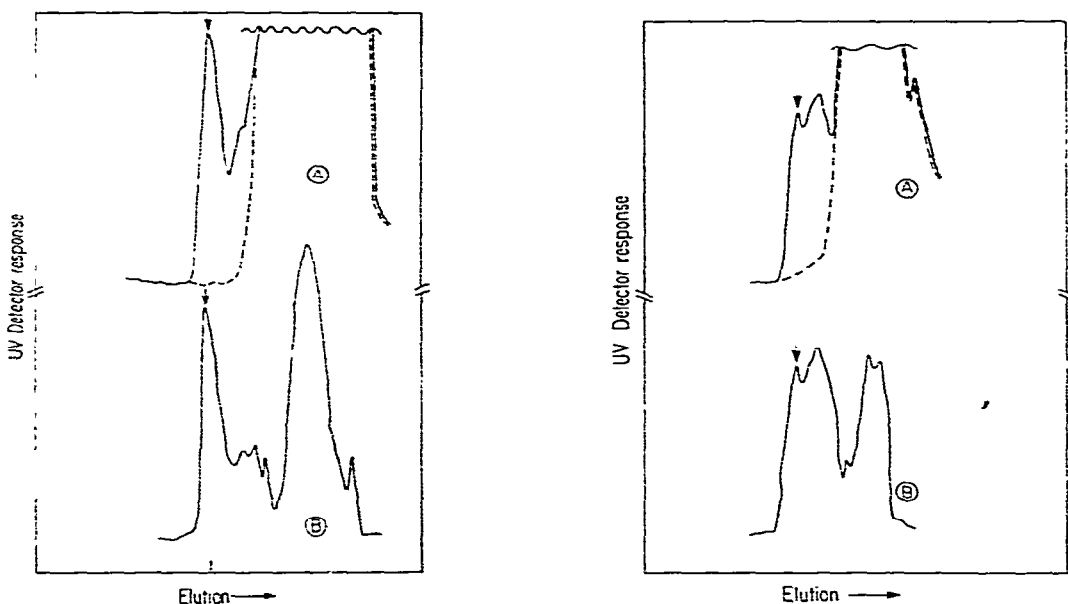


Fig. 1. Gel permeation chromatograms of (A) QS 2598A paraffinic oil (solid line) and QS 2598A base oil (without flow-improver) (broken line) and (B) flow-improver (0.4% tetrahydrofuran). Injection volume, 100 μ l. UV detection at 230 nm. Sensitivity, 0.5 a.u.f.s.

Fig. 2. Gel permeation chromatograms of (A) Voltesso 35 naphthenic oil (solid line) and Voltesso 35 base oil (without flow-improver) (broken line) and (B) Paraflow 149 (0.1% tetrahydrofuran). Injection volume, 100 μ l. UV detection at 230 nm. Sensitivity, 0.5 a.u.f.s.

Fluorescence detection was also used to analyse Paraflow 149 in Voltesso 35 (Fig. 3). Only the polymer part of Paraflow is fluorescent, probably owing to its naphthalene-type structure; the oily part is not fluorescent. The flow-improver of the QS 2598A paraffinic oil cannot be analysed with this type of detection as its polymer part is not fluorescent.

Calibration graphs relating the polymer peak height to the flow-improver con-

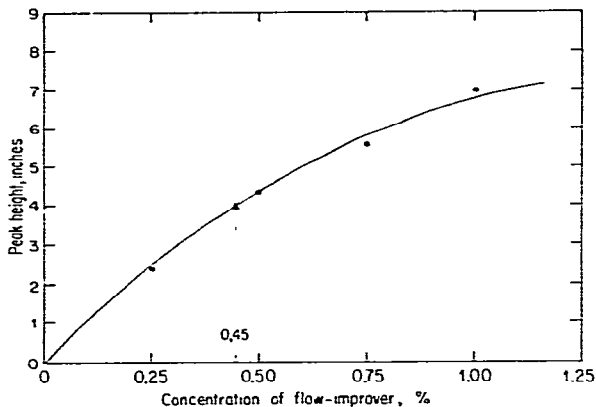
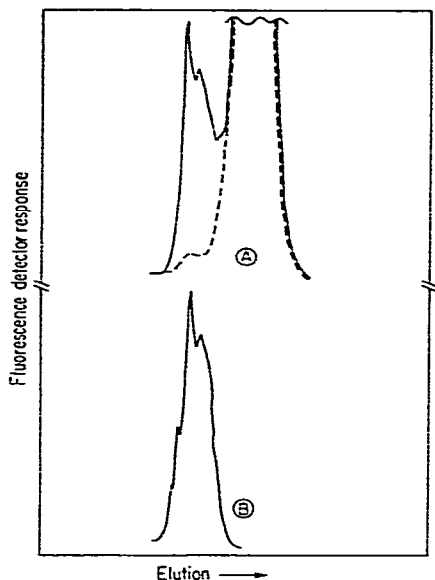


Fig. 3. Gel permeation chromatograms of (A) Voltesso 35 (solid line) and Voltesso 35 base oil (without flow-improver) (broken line) and (B) Paraflow 149 (0.1% tetrahydrofuran). Injection volume, 70 μ l. Fluorescence detection. Sensitivity, 2.0 a.u.f.s.

Fig. 4. Calibration graph for flow-improver content in QS 2598A paraffinic oil (UV detection).

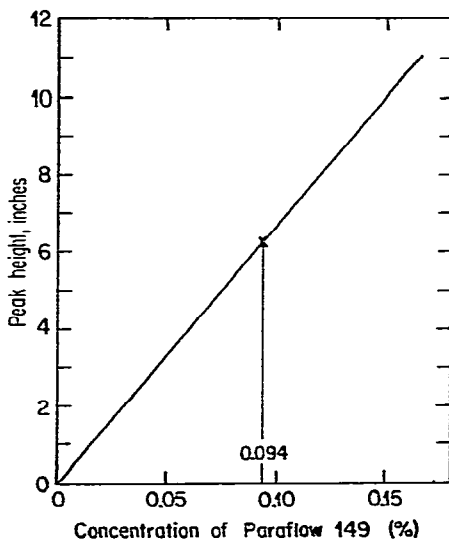
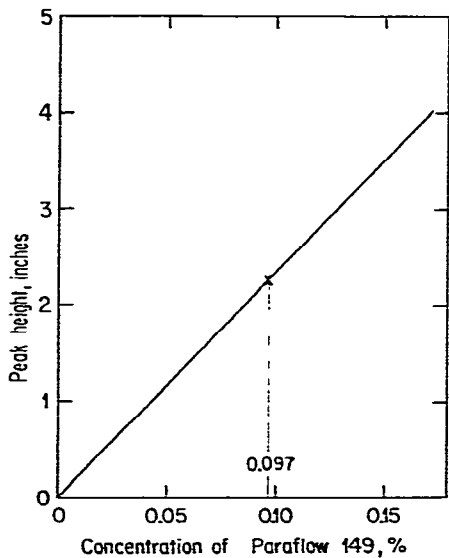


Fig. 5. Calibration graph for Paraflow 149 in Voltesso 35 (UV detection).

Fig. 6. Calibration graph for Paraflow 149 in Voltesso 35 (fluorescence detection).

centration in transformer oil were constructed using standard mixtures containing known amounts of flow-improver in the corresponding base oil. These curves are shown in Figs. 4-6; 0.45% (w/w) of flow-improver was found in the QS 2598A paraffinic oil and 0.097 and 0.094% (w/w) of Paraflow 149 were found in Voltesso 35 using the UV and fluorescence detectors, respectively. The accuracy with replicate injections is $\pm 3\%$.

Analysis of aged oils

When transformer oils are subjected to oxidation or corona discharges, polar degradation products and polymers of intermediate molecular weight are formed, which tend to broaden the main transformer oil peak on the chromatograms. However, these products do not interfere with the polymer peak of the flow-improver, as can be seen in Fig. 7, where samples of QS 2598A paraffinic oil and the corresponding base oil were subjected to the same corona discharge conditions (9 kV, 5 days, in air): at the peak position (arrow) there is no absorption due to degraded oil (broken line), although the main oil peak is much broader than in the new oils (see Fig. 1A). Similar observations were made in the case of oxidation and of Voltesso 35.

Application to aged transformer oils

Concentrations of flow-improvers in oils subjected to corona discharges and oxidation for various periods of time are shown in Fig. 8. The variations observed are very small and almost within the precision range. Flow-improver additives thus appear to be stable towards degradation.

With Paraflow 149, however, there is a sharp change in fluorescence activity (Fig. 9), indicating that the naphthalene structure has somehow been modified.

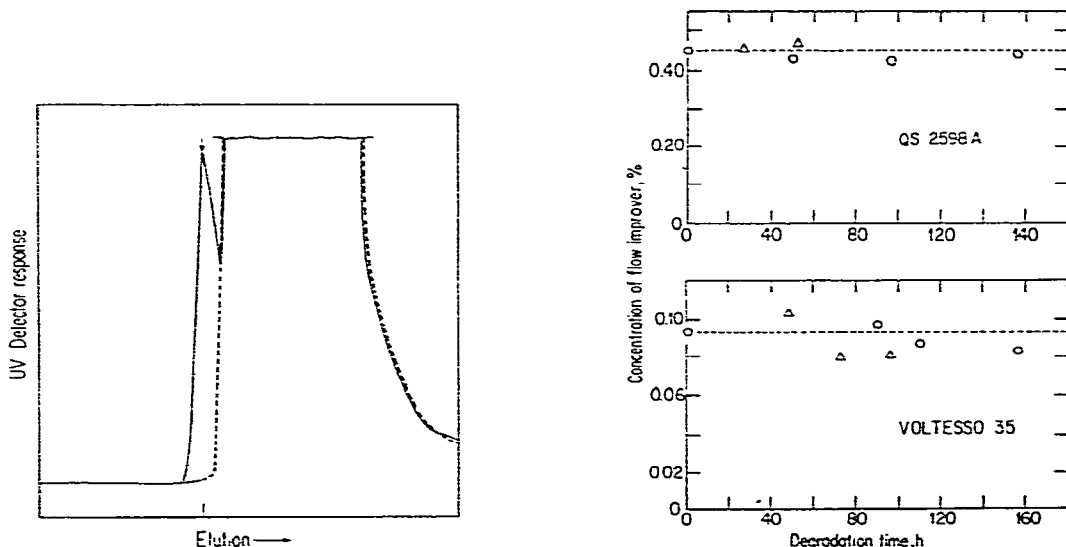


Fig. 7. Gel permeation chromatograms of oil samples subjected to corona discharges (5 days in air at 9 kV): solid line, QS 2598A; broken line, QS base oil.

Fig. 8. Concentration of flow-improver (UV peak) as a function of degradation time: Δ , corona; \circ , oxidation.

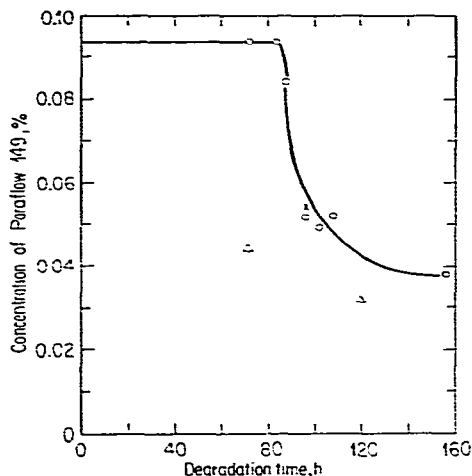


Fig. 9. Concentration of Parafflow 149 (fluorescence peak) as a function of degradation time: Δ , corona; \circ , oxidation.

CONCLUSIONS

GPC can be used for the analysis of polymer flow-improvers in electrical insulating oils. Oil degradation products have been shown not to interfere under the experimental conditions used. The method is accurate to $\pm 3\%$ and is reproducible. Concentrations of flow-improving additives in the new naphthenic and paraffinic transformer oils used by Hydro-Québec were found to be close to 0.1% and 0.45%, respectively, and not to change significantly after oxidation or electrical discharges.

ACKNOWLEDGEMENTS

The Canadian Electrical Association is gratefully acknowledged for supporting part of this work. Special thanks are also due to the Imperial Oil Company for providing samples of oil and flow-improving additives and to Mrs. L. Regnier for reviewing the manuscript.

REFERENCES

- 1 S. D. Myers, J. J. Kelly and R. H. Parrish, *A Guide to Transformer maintenance*, TMI Publ., Akron, OH, 1981.
- 2 L. E. Lorensen, *ACS Symp. Polym. Lubr. Oil. Atlantic City. Sept. 9-14, 1962*.
- 3 M. Duval and C. Lamarre, *IEEE Trans. Electr. Insul.*, EI-12 (1977) 340.