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NON-EXTRACTABLE POLYMER COATINGS (MODIFIED SUPPORTS) FOR CHROMATOGRAPHY

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SUMMARY

The technique of producing extremely thin, non-extractable polymer layers on diatomaceous supports has been extended from Carbowax 20M to a variety of polar and non-polar polymers commonly used in gas–liquid chromatography.

INTRODUCTION

We have described in an earlier paper[1] the unexpected chromatographic performance of a non-extractable, very thin film of Carbowax 20M on Chromosorb W (or other silicic supports). This phase yields sharp, symmetrical peaks with short retention times for a variety of polar compounds. High carrier gas flows can be used without loss of chromatographic efficiency, and decomposition is at a minimum.

Our failure to extract these chromatographic properties from the packing (*e.g.* with methanol during a month in a Soxhlet) prompted questions regarding the nature of the bonding between the—obviously present—polymer film and the diatomaceous support. Our working hypothesis, at that time (and now), was that significant parts of the long Carbowax 20M molecule had assumed positions of minimum potential energy on the silicic surface—*i.e.* as stretched-out[2] and probably oriented chains—and that the combined effects of a large number of intermolecular bonds caused all extraction attempts to fail.

Carbowax 20M which had been extracted from heat-treated materials did not appear different from the initial polymer by both IR and gel permeation chromatography; and mass spectra of the column bleed were similar to bleed from conventional Carbowax 20M columns. Yet, a variety of possible reactions such as oxidation, cross-linking, support-bonding, etc., could not be excluded with confidence—especially since Carbowax 20M differs from other polyethylene glycols[3]. For this reason, and with an eye on possible analytical applications, we selected a number of heat-stable, long-chain common chromatographic liquid phases of various chemical structures. These were heat-treated, extracted and tested with polar and non-polar compounds.

EXPERIMENTAL

General procedure

Celite 545 or Chromosorb W, 100–120 mesh, was acid-washed in a Soxhlet (Kontes, Vineland, N.J., U.S.A., Model K-585100) by refluxing with concentrated hydrochloric acid. Acid washing was considered complete when a fresh portion of HCl remained colorless after refluxing overnight. The diatomaceous support was washed to neutrality with distilled water, rinsed with acetone, and dried by rotary evaporation at 75°.

About 35 g of the acid-washed support were then coated with 6% of the respective liquid phase by the conventional rotary evaporation technique. The coated support was divided into portions and each portion, except one, was filled into a 50 cm×3 cm I.D. glass tube with Clearfit joints (Fairfield, N.J., U.S.A.), one end connected to a supply of highly purified nitrogen and the other end connected to a capillary immersed in water. The filled tube was placed in a tubular furnace and swept for 1 h with a fast stream of nitrogen at room temperature to replace all the oxygen, after which the nitrogen flow was turned down to a minimum such that a slow succession of bubbles could be observed at the tip of the capillary. The temperature was then raised to the desired level during 3–4 h and kept constant for about 18 h. After cool-down to room temperature, the heat-treated phase (as well as the non-heated portion) were exhaustively extracted in Goldfisch equipment (Fisher Scientific, St. Louis, Mo., U.S.A.) for 1–2 days with appropriate solvents.

The extracted supports were tested in 50 cm×4 mm I.D. glass columns in a Perkin-Elmer Model 800 (Perkin-Elmer, Norwalk, Conn., U.S.A.), with mixtures of *n*-alkanes and *n*-alkanols. After the gas chromatographic runs, a small amount of the column packing was removed for analysis. Part of this material was ignited (3 h at 1000° in air) to determine polymer loss, and part of it was sent to a commercial laboratory for elemental analysis, accompanied by instructions to dry the samples in vacuum at 150° for at least 4 h prior to analysis.

Heat-treatment and extraction

Temperature profiles on the effects of heat treatment at different temperatures were established for each of the phases. These temperatures covered approximately a 100° range around the recommended maximum operating temperature. Heated packings were extracted with solvents expected to give maximum solubility of the liquid phase, and sometimes with a succession of different solvents. Apiezon L (Applied Science Lab., State College, Pa., U.S.A.) was heated at 240°, 280°, 300° and 350°, followed by extraction with methanol for 18 h, and benzene for another 18 h. Chromatographic grade GE SE-30 (Applied Science Labs., State College, Pa., U.S.A.) was heated at 335°, 350° and 400°, and extracted with chloroform for about 36 h. The phase AN-600 (Analabs, North Haven, Conn., U.S.A.) was heat-treated at 300°, 320° and 350°, and extracted with acetone for 36 h, followed by isopropyl alcohol for another 36 h. Stabilized ethylene glycol adipate (Analabs) was heat-treated at 180°, 200°, 220° and 250° and extracted with acetone for 36 h. Dexsil 300 (Analabs, North

Haven, Conn., U.S.A.) was heat-treated at 380°, 440°, 500° and 550°, but the experiment was terminated owing to the apparently not uncommon misfortune of purchasing a bad batch of this expensive material. Linear polyethylene (NBS Standard) was heated at 260° and extracted with toluene for 24 h. "Linear Carbowax 20M" (a pure polyethylene glycol of molecular weight 20,000; courtesy of J. J. Stratta, Union Carbide, New York, N.Y., U.S.A.) was treated similar to the procedure for Carbowax 20M (ref. 1).

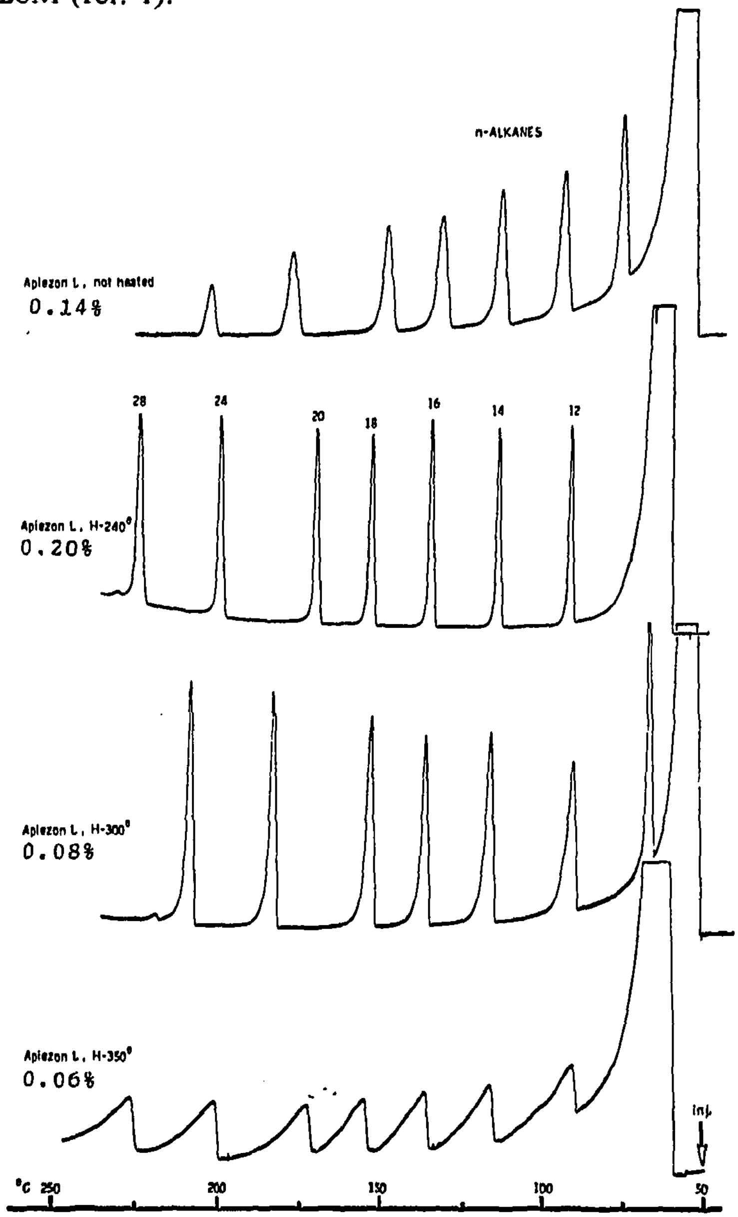

Fig. 1. Effects of heat treatments on the extractability and chromatographic performance of Apiezon L (a hydrocarbon product) coated on diatomaceous earth.

RESULTS AND DISCUSSION

Fig. 1 shows the temperature profile for Apiezon L. Figs. 2–6 compare only the phase heated at the "best" temperature with the blanks, which are merely coated and extracted materials. The percent polymer loads given in the figures are averages calculated from the elemental analyses for carbon and hydrogen. Our own ignition gave 0.2–0.4% polymer losses. Similar to elemental analysis, this procedure appears to operate at its limit of capability and the quoted values seem, at best, to indicate the maximum possible polymer load.

In this context, the examined polymers gave results comparable to those obtained from Carbowax 20M (which showed less than 0.2% load[1]). The "linear" Carbowax 20M (Fig. 6) was included in this study to demonstrate that the presence of a linkage between polyethylene glycol moieties (by a proprietory diepoxide) in regular Carbowax 20M was not responsible for the observed effects. The gas chromatographic performance of the other new phases was, perhaps, not as good as could have been hoped for, but the expected effects of heat-treatment could be clearly demonstrated. It appears reasonable, therefore, to assume that Carbowax 20M is not a phase *sui generis* in this regard, but simply represents one particular, good example of a general phenomenon.

Various types of comparatively feeble intermolecular forces, through a favorable

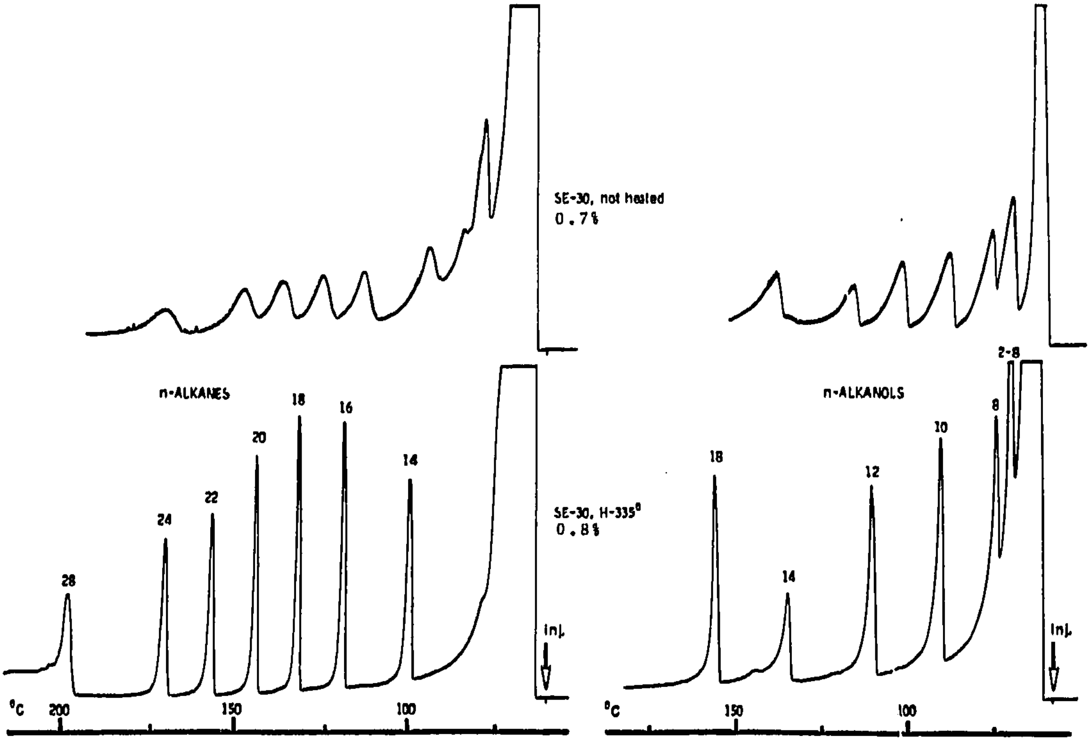

Fig. 2. Effects of heat treatment on the extractability and chromatographic performance of a layer of SE-30 (a dimethylpolysiloxane).

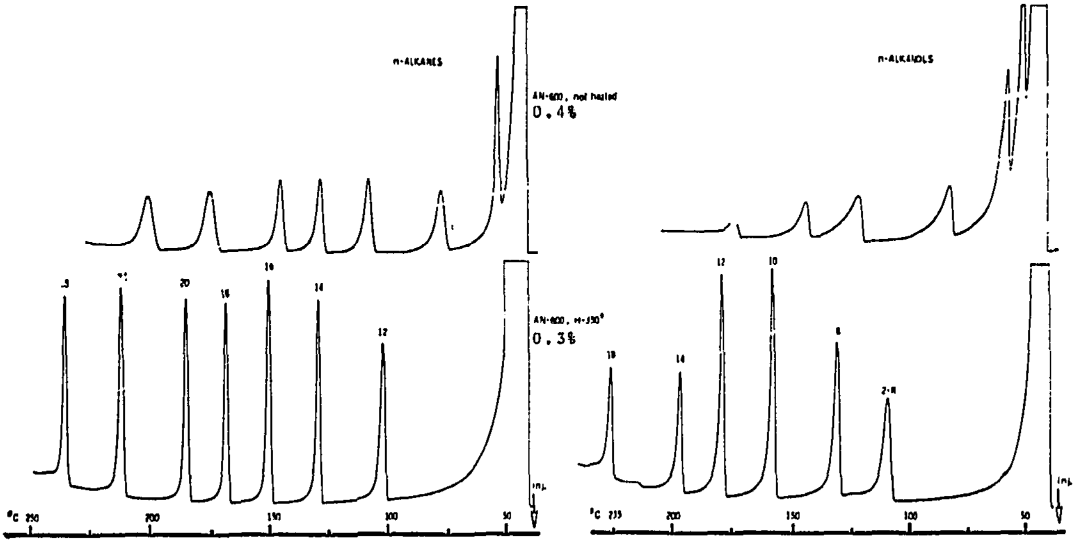

Fig. 3. Effects of heat treatment on extractability and chromatographic performance of a layer of AN-600 (a 2-cyanoethyl(methyl)polysiloxane).

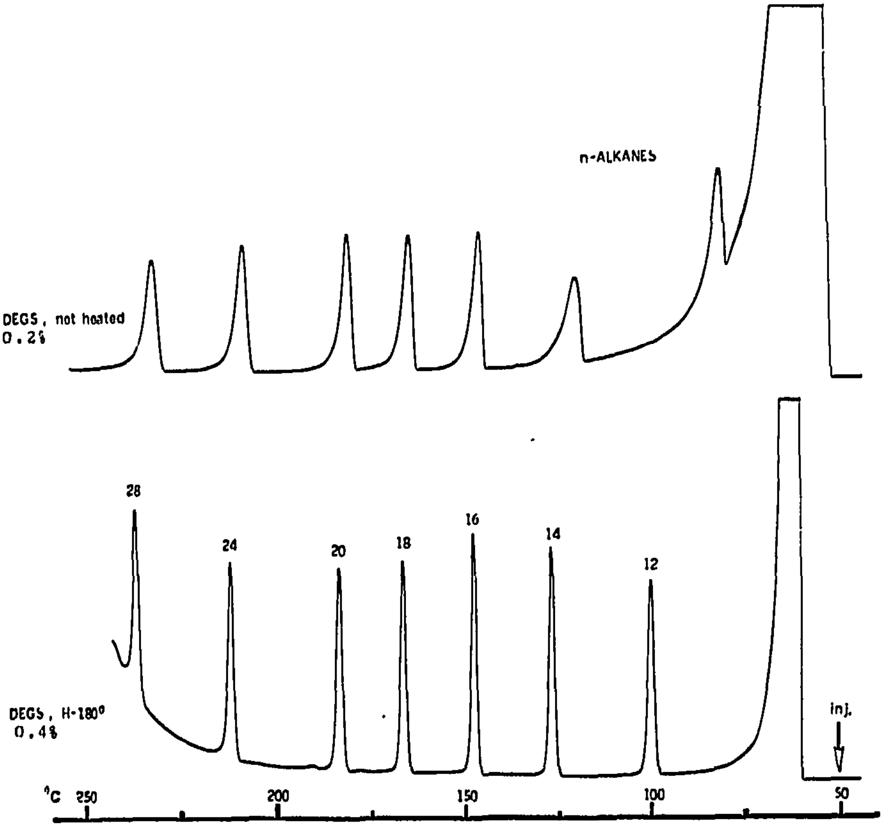

Fig. 4. Effect of heat treatment on the extractability and chromatographic performance of a layer of polydiethylene glycol succinate.

steric arrangement and the summation of a large number of weak bonds, can conceivably bring about a "better" phase than much stronger, but isolated chemical bonds. For example, a molecule of Carbowax 20M could have formed two chemical bonds to the surface (through condensation of the two terminal hydroxyls with two surface silanols). However, such bonds are generally hydrolyzed by alcohols under mild conditions, and should have not survived the protracted extraction by methanol at boiling point temperatures. The summation of "physical" bonds between a long-chain molecule and its environment is a common approach in polymer adhesion chemistry; and it is our contention that it may be useful for explaining the effects reported in this paper as well.

While "chemical" cross-linking or support-bonding cannot be ruled out with some phases (the stabilizer in DEGS is a cross-linking agent, phosphoric acid; silicones are notorious for rearrangements, etc.), others, such as Apiezon L and especially linear polyethylene, could hardly be suspected of such a behaviour. Thus the obtained results appear to support our original hypothesis of optimal physical bonding between polymer chains and the silicic surface.

From an analytical point of view, these and similar phases could find application in several areas of chromatography. Foremost, perhaps ,would be the gas chroma-

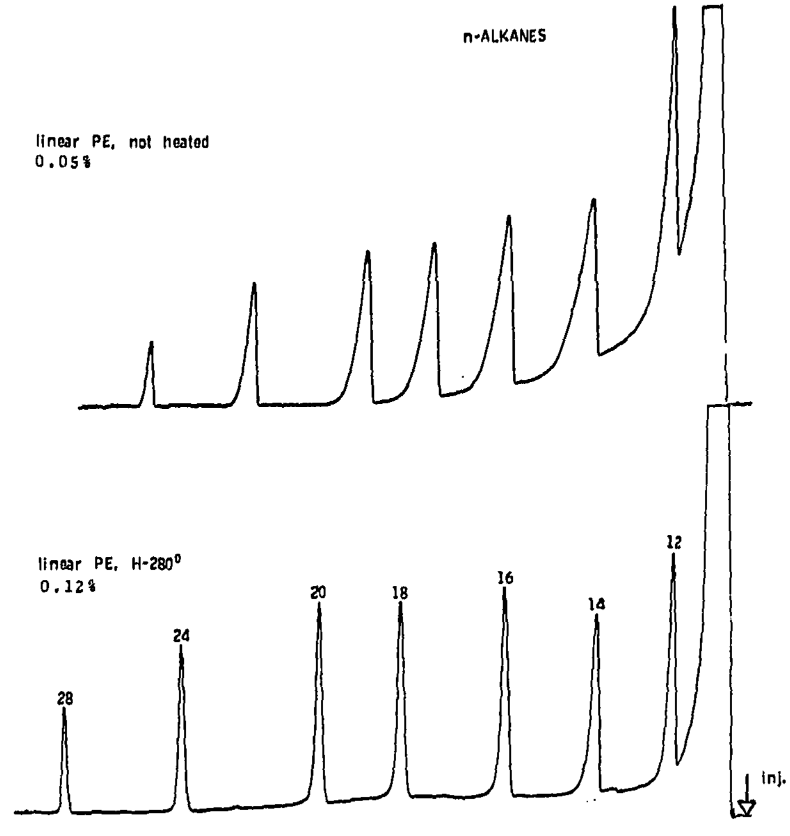

Fig. 5. Effects of heat treatment on a layer of linear polyethylene

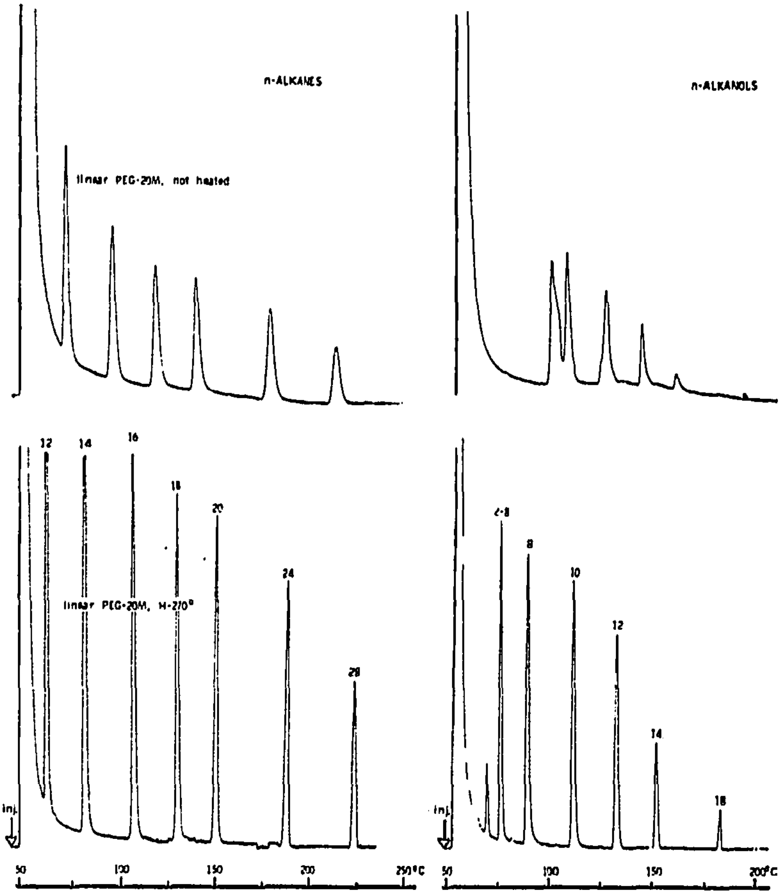

Fig. 6. Effects of heat treatment on a layer of linear Carbowax 20M.

tographic trace analysis of late-eluting, polar compounds. In this area, which includes samples of environmental or biochemical origin, the pronounced reduction in bleed, retention time and retention temperature afforded by the extremely thin layers may prove a distinct advantage. A second area of possible application would be liquid chromatography, where a modification or deactivation of adsorbent surfaces is often desirable.

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