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## ALTERNATIVE METHOD FOR BONDING POLYMER LAYERS TO CHROMATOGRAPHIC SUPPORTS

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### SUMMARY

An alternative method for producing “bonded” (= non-extractable) layers of polymers on diatomaceous supports has been developed. Whereas the original method used a treatment of the support with the neat polymer, the new one uses solution-coating in a refluxing hydrocarbon. Judged by the gas chromatographic performance of the packings obtained from the most useful of the polymers, Carbowax 20M, the two methods yield equivalent products. The new method, though restricted in scope, is the faster and more gentle one of the two.

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### INTRODUCTION

Some years ago our group described a procedure for “bonding” polymer layers to silicic supports used traditionally in gas chromatography (GC)<sup>1</sup>. These layers were quite thin (close to monomolecular) and could not be removed by weeks of continuous extraction with appropriate organic solvents. Such layers were produced, by coating, heat treatment, and extraction, from various polymers including ether, ester, siloxane and pure hydrocarbon structures and an hypothetical explanation of this unexpected phenomenon was suggested at that time. Further work clarified some physicochemical properties of these “modified surfaces”<sup>2</sup> and explored their direct<sup>3</sup> and indirect<sup>4</sup> use in GC. Since then, such materials have apparently become commercially available<sup>5–7</sup>. The basic bonding process, however, has not been further investigated.

Such “bonding” of polymers must, it is reasonable to suggest, occur in many systems and under many circumstances —although it may be rarely recognized as such. Chromatography happens to be an area where it is conveniently observed; but it may not be the only nor the most important one. It was in chromatography, however, where good use has been made of the heat treatment—extraction procedure, especially in conjunction with capillary columns<sup>8–10</sup>. Of particular interest in this

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regard is the approach taken by Grob and Grob<sup>11</sup>, who used a multistep coating with a very dilute PG 20M solution.

The heat treatment, this crucial step in the preparation of chromatographic phases, continued to attract our interest for obvious reasons. In the original procedure, a thick polymer layer (*e.g.* 6% on Chromosorb W) was heated in a nitrogen atmosphere. All but the "bonded" layer (*e.g. ca.* 0.2% on Chromosorb W) was then removed by extraction. This procedure was simple and its results were reproducible. The heat-treatment was necessary to obtain a non-extractable layer, as was shown by many experiments where extraction without prior heat-treatment easily removed the chromatographic properties of the support.

Yet, on rare occasions materials were obtained which showed some evidence of bonding even in the absence of heat-treatment. Such bonding, however, was not reproducible. A study was done on the Carbowax 20M-acid-washed Chromosorb W system and indicated that the polarity of the solvent (in which the polymer was dissolved for the original coating procedure) was of some importance, as was the rate at which the polymer was added<sup>12</sup>. Neither effect, however, could be clearly defined at that time.

Polymer adsorption from solution is a well studied phenomenon; for instance, monomolecular polyethylene glycol layers on graphitised carbon black have been produced in this manner<sup>13</sup> for chromatographic purposes. Adsorbed polymer layers are, of course, extractable in most if not all cases. It was therefore interesting to attempt to find conditions under which polymers would be irreversibly adsorbed ("bonded") from solution; an effect which would have to be demonstrated by their resistance to extraction by various solvents for any reasonable length of time.

There were several reasons for this interest. First, a heat treatment in solution might lead to a different polymer distribution on the support surface. Second, some selectivity in terms of polymer structure, *e.g.* chain length, could become apparent. Third, the support particles would be equally accessible from all sides, rather than being held in a fixed position relative to each other and to the nitrogen stream, as in the original procedure. Fourth, treatment in solution may be considered a less severe approach than the original heat-treatment, minimizing any chemical change of the bulk polymer phase. Fifth, most of the polymer could be easily removed by decanting the solvent and commencing extraction with the support still wet—thus denying the polymer the opportunity to dry out, cross-link with traces of oxygen, etc.

#### PRELIMINARY EXPERIMENTS

These were done with the Carbowax 20M-Chromosorb W system and involved the slow addition of a polymer solution to a suspension of Chromosorb in a hot, (generally) refluxing solvent, in a nitrogen atmosphere. The solvents used were ethylene glycol, di-*n*-butyl phthalate, tetralin and various *n*-hydrocarbons. In these experiments, a *low polarity* of the solvent and a *high temperature* favored good chromatographic performance of the exhaustively extracted support, indicating the presence of a non-extractable polymer layer. This is consistent with the idea of increased adsorption and easier orientation, respectively, of the polymer chains on the surface.

The addition of considerably larger amounts of Carbowax than were bonded,

proved beneficial. This was checked by GC testing for retention, asymmetry and HETP values for a variety of alcohols. Whether an increased initial adsorption and/or polymer fractionation is responsible for this effect has not been investigated.

From the experiences gained in these preliminary experiments, a simple apparatus was constructed and a technique developed to produce several types of modified supports.

## EXPERIMENTAL

The GC support, Chromosorb W or P, was cleaned as described earlier<sup>14</sup> by a one-day extraction with boiling 6 *N* hydrochloric acid, a two-to-four-day treatment with hydrogen chloride gas at 850°, a final one-day extraction with boiling 6 *N* hydrochloric acid, washes with water, very dilute sodium hydroxide, and double distilled water to neutrality, and a drying step overnight in a vacuum oven at 160°.

Then it was transferred to the set-up shown in Fig. 1 and suspended in the chosen solvent (even numbered *n*-hydrocarbons from dodecane to eicosane as obtained from Chemical Samples, Columbus, Ohio, U.S.A.). A brisk stream of nitrogen, prepurified grade, (freed of oxygen and water in a scavenger cartridge obtained from Supelco, Bellefonte, Pa., U.S.A.) was turned on well before the heating began. The nitrogen left the reflux condenser through a long tube (to prevent back-diffusion of atmospheric oxygen), terminating in an exhaust duct.

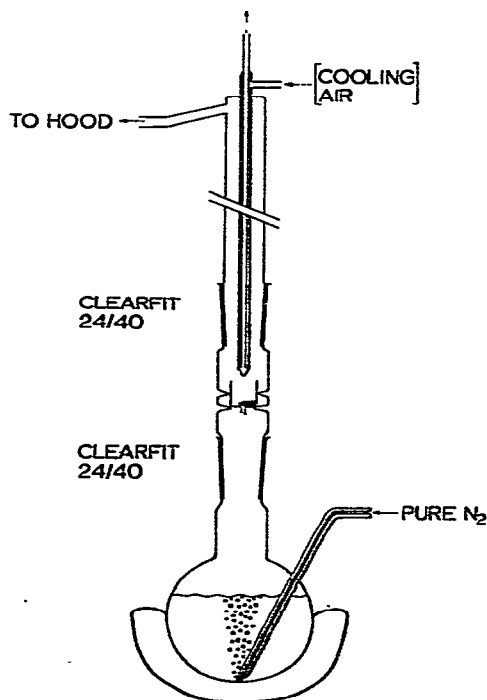


Fig. 1. Apparatus used for "bonding" polymers to chromatographic supports.

The polymer, about 5% in weight of the Chromosorb, was put into a little storage vessel whose shape varied according to the polymer used. When heating was started, most of the refluxing solvent liquified on the wall of the condenser, and ran back into the flask without touching the polymer. Later, the cold finger was cooled by air and the condenser wall insulated, to drip solvent into the vessel and bring dissolved or melted polymer dropwise down into the flask. After all polymer had been added (10–30 min in most cases), refluxing was continued for a total 6 h of reaction time. After allowing it to cool under nitrogen to a manageable temperature, the solvent was decanted and the coated support washed a few times with an appropriate solvent, *i.e.*, one miscible with the high-boiling hydrocarbon and known to dissolve the polymer used. The material was then extracted at, or close to, boiling point temperatures with the most efficient solvent (or a sequence of solvents) in a Soxhlet (Kontes Model K585100) for at least 48 h. In later experiments an extractor of our construction<sup>15</sup> was used, which allowed us to reduce this time to 20 h and to conduct the extraction under nitrogen, if considered desirable.

The coating apparatus was designed to provide a gently stirred, oxygen-free system, in which a controlled addition of polymer could be conducted without introducing any lower-boiling solvent. Clearseal joints (Wheaton, Millville, N.J., U.S.A.) provided the necessary leak-tightness without a lubricant—which, for obvious reasons, could not be used.

After extraction, the phases were dried for *ca.* 3 h in vacuum at *ca.* 40°, packed into short glass columns (1 m × 1.8–2 mm I.D.) and tested in a Shimadzu Model 4B gas chromatograph, with flame ionization detection of hydrocarbons, alcohols, and other compound types.

A variety of polymers was thus processed; among them ester, ether, thioether, siloxane, aromatic and aliphatic structures. Tetralin was occasionally substituted for the hydrocarbons as a solvent if the latter posed solubility problems.

For a few comparisons, regular gas-liquid chromatographic (GLC) phases of 5% load were prepared from the same materials by conventional rotary evaporation, and subjected to the same exhaustive extraction as their “bonded” counterparts.

Polymers were obtained from Chromatographic Specialties, Brockville, Canada (polyethylene glycol adipate (PEGA), Carbowax 20M, SE-30, OV-101, OV-210, polyphenyl ether-6 ring, and others), Aldrich, Milwaukee, Wisc., U.S.A. (2,6-dimethylpolyphenoxyphenyl ether, linear and branched polyethylene, polyphenylsulfide, polyethylene oxide and others), and the U.S. National Bureau of Standards, Washington, D.C., U.S.A., (linear polyethylene). Apiezon L was purified by column chromatography on silica gel with hexane as solvent.

## RESULTS

Carbowax 20M, the polymer mainly studied, gave modified supports equivalent to the best ones produced by the old method<sup>1</sup> when coated in refluxing hexadecane. Fig. 2 shows a standard mixture of alcohols, contrasted with the same mixture run on an extracted, regular GLC packing (*i.e.* an almost bare support).

A similar picture is shown by PEGA in Fig. 3. The extracted *regular* GLC packing causes extensive decomposition of the alcohols as expected.

Fig. 4 shows a hydrocarbon chromatography on a modified support based on

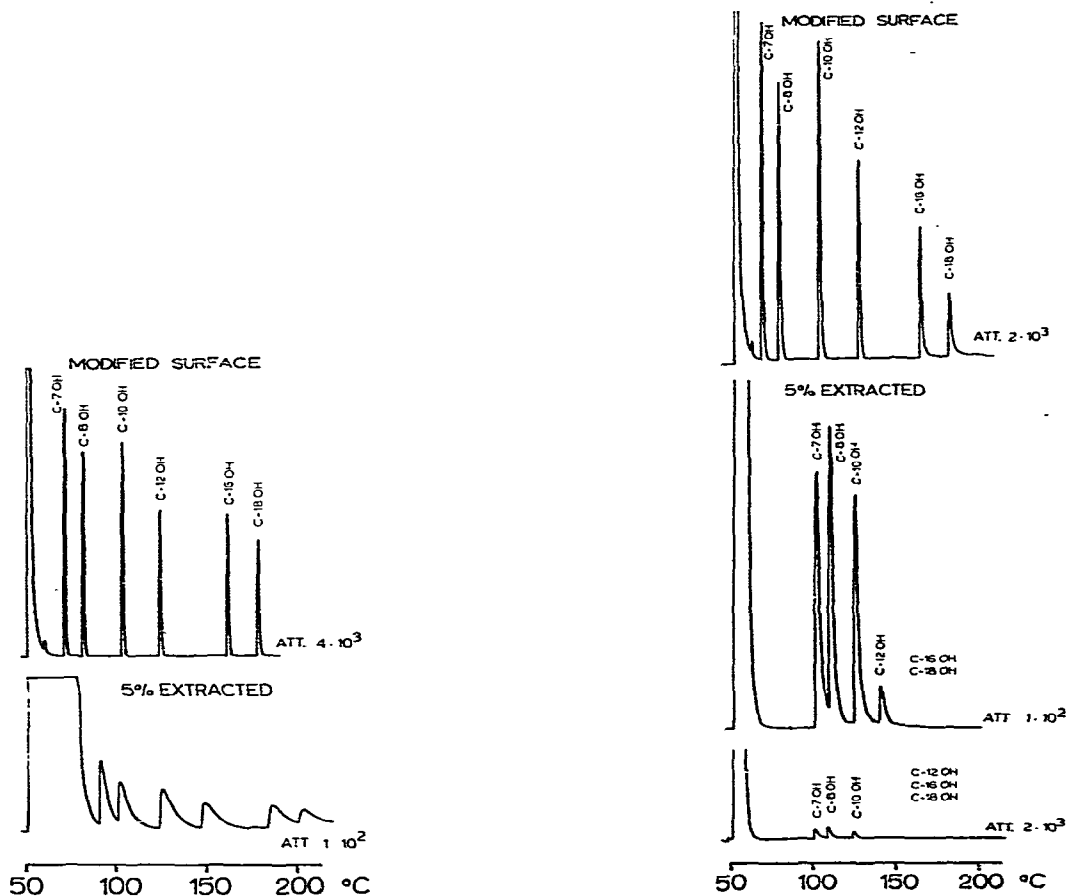


Fig. 2. Upper trace: Gas chromatography of normal, primary alcohols on Chromosorb W, 100–120 mesh, modified by a layer of Carbowax 20M, as produced by coating in refluxing hexadecane, and extracting 20 h with methanol at boiling point temperatures. Lower trace: Same chromatography on a similarly extracted, regular 5% Carbowax 20M GLC packing. Note the different attenuation.

Fig. 3. Upper trace: Gas chromatography of primary alcohols on Chromosorb W, 100–120 mesh, modified by a layer of PEGA; as produced by coating in refluxing dodecane and extracting 20 h with methanol. Lower traces: Same chromatography at two different attenuations on a similarly extracted, regular 5% PEGA GLC packing.

(purified) Apiezon L. Especially notable are the low elution temperatures of the *n*-alkanes.

Fig. 5 shows some chromatographies on a support modified by polyethylene oxide (Aldrich). Although alcohols do not show up as nicely as on the chemically related Carbowax layer, the phase may be useful for other compounds. Its heat-stability is good, as shown by surviving (accidental) exposure to 300° overnight.

Other polymers gave mixed results. The best chromatographic performances were obtained from OV-210 coated in tetradecane and extracted in toluene, less well performed polyphenylene sulfide coated in tetraline and extracted in toluene. Aromatic polymers like the 6-ring polyphenyl ether or 2,6-phenyl-*p*-phenylene oxide gave un-

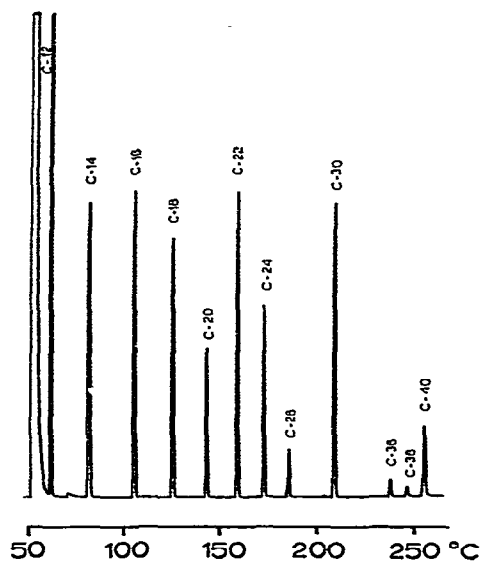


Fig. 4. Gas chromatography of various amounts of normal alkanes on Chromosorb W, 100-120 mesh, modified by a layer of Apiezon L (purified from the commercial product by column chromatography with hexane on silica gel); as produced by coating in octadecane and extracting 20 h with hexane at boiling point temperatures.

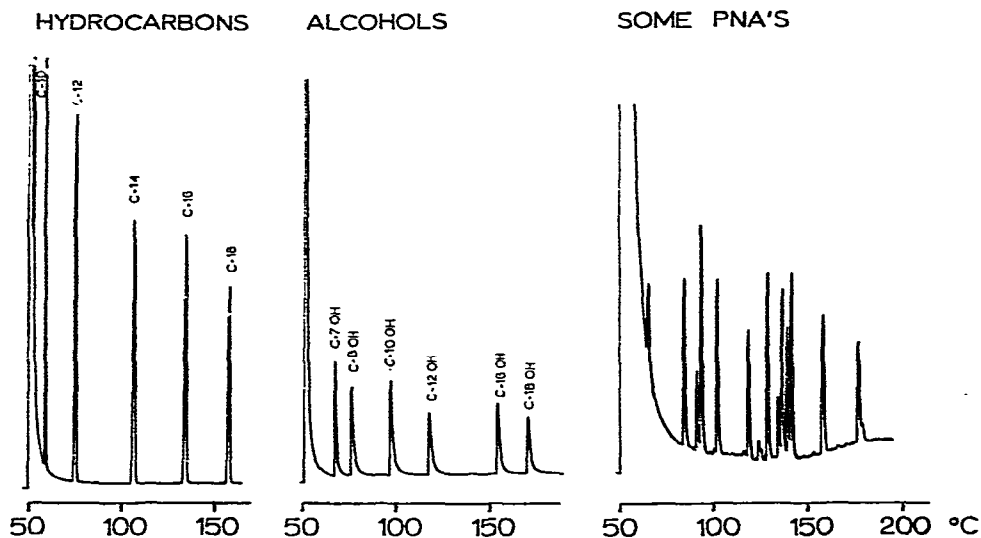


Fig. 5. Gas chromatographies of standard *n*-hydrocarbon, *n*-alcohol, and polynuclear aromatic (PNA) mixtures on Chromosorb W, 100-120 mesh, modified by a layer of polyethylene oxide; as produced by coating in hexadecane and extracting for 20 h with methanol at boiling point temperatures.

satisfactory results as did, somewhat surprisingly, some polydimethylsiloxanes. Various polyethylenes gave results that were not quite reproducible; this matter was not further investigated.

## DISCUSSION

The fact that some of the tested liquid phases gave unsatisfactory chromatographic results was to be expected from the rather indiscriminate approach used toward widely differing polymers in this study. Furthermore, certain chemical structures will "bond" easier than others<sup>16</sup>; and a thorough investigation of each separate case was never carried out.

The important fact, however, is that several polymers, notably the standard Carbowax 20M and the unpolar Apiezon L, performed just as well in the new as in the old method. One could speculate that the chances for the polymer to stick permanently to the support were substantially reduced if the heat treatment was performed with the particles being suspended in a dilute polymer solution, rather than being in direct contact with a bulk liquid phase as in the original method. Furthermore, one should also note that in the new procedure the polymer solution was decanted while still warm, the support washed, and immediately subjected to exhaustive extraction—a procedure designed to remove as much polymer as fast as possible while keeping it from drying out.

No thorough study was performed of possibly important parameters such as the rate of polymer addition or the time of refluxing. Also, tetraline and the *n*-alkanes were the only solvents tested to any extent; once it became obvious that more polar solvents would not perform as well.

The method has therefore obvious limitations in its present form. The boiling points of the commercially available hydrocarbons define the temperatures at which the coating procedure can be most conveniently performed. Some polymers do not dissolve adequately in hydrocarbons, even at high temperatures.

The advantages of the new method are its speed, simplicity and gentleness — all relative to the original approach, of course. With the standard polymer, Carbowax 20M, reproducibility was excellent. Various batches yielded the same chromatographic performance and no "bad" batch was ever obtained. As far as tested, these materials were equivalent to the best batches produced by the old method.

## ACKNOWLEDGEMENTS

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