NOTES.

Piston Oils of Low Spreading Pressure. By Alfred Norris and T. W. J. Taylor.

To maintain a constant pressure in experiments where a surface film is transferred from a water surface to a solid, it is usual to use a piston oil separated from the film by a waxed silk thread (Blodgett, *J. Amer. Chem. Soc.*, 1934, **56**, 495; 1935, **57**, 1007, etc.). For pressures of the order of 30 dynes/cm. purified oleic acid can be used, and at about 15 dynes/cm. castor oil. At about 9 dynes/cm. Langmuir has used tritolyl phosphate, and for lower pressures partially oxidised indicator oil (*J. Amer. Chem. Soc.*, 1937, **59**, 2400).

In order to have a greater control on the pressures at which films can be transferred, we have tried several binary mixtures of a compound with no tendency to spread with one which has a high spreading pressure. A satisfactory mixture was found to be that of high-boiling paraffin with ethyl myristate. It was anticipated that, when such a mixture was spread on a water surface, the composition of the film would not be the same as that of the liquid which remains as a droplet, so that, to maintain the composition of the droplet effectively constant, it would be necessary to have a considerable excess of the mixture on the surface. The pressure should then be independent of moderate changes in surface area. This anticipation proved correct: as very small drops of the mixture were successively placed on about 200 sq. cm. of water surface, the pressure registered on an Adam's surface balance slowly changed to a constant value, and this value was unchanged when the surface was reduced or increased in area.

The paraffin was a high-quality medicinal paraffin, which had been heated to 150°/10 mm. to remove spreading constituents, and it showed no sign of spreading on a water surface; the ethyl myristate was a pure specimen spreading at a pressure of 20·7 dynes/cm. The liquids were too viscous to mix rapidly or to be handled easily, and hence solutions of accurately known strength (approximately 10%) of each in light petroleum (b. p. 60—70°) were prepared and mixed in various proportions, and the light petroleum evaporated. The results were:

Ethyl myristate, %	0	10·0	16·5	33·0	49·0	65·5	100
Pressure, dynes/cm.	0	5·0	8·5	11·1	14·7	17·0	20·7

A binary mixture which gives control over spreading pressure has been described by Adam (*Proc. Roy. Soc.*, 1937, *B*, **122**, 134); it consists of a hydrocarbon oil and *n*-dodecyl alcohol. With these components the pressure rises from zero to 22 dynes/cm. as the alcohol content is increased from 0 to 1%. The mixture we describe is not so sensitive to concentration changes, and provides a convenient method of obtaining a wide range of pressure at intervals as small as may be desired, without having recourse to a large variety of substances.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, September 26th*, 1938.]

Fractional Distillation of Mixtures of Constant Boiling Point. By ROBERT WRIGHT.

THE composition of the distillate from a constant-boiling binary mixture may be altered by changing the pressure at which the distillation takes place, or by the addition of a third substance which has a selective action on one of the two constituents. This action may be chemical, as in the production of absolute alcohol by means of lime, or it may be simply due to the lowering of the vapour pressure of one constituent, relative to that of the other, resulting from the greater solubility of the added solute in the first constituent. The latter is the principle of the method first suggested by Young (J., 1902, **81**, 710) for the dehydration of alcohol by the addition of benzene. When benzene is added to constant-boiling 95% aqueous alcohol it decreases the vapour pressure of the alcohol, so the first fraction of the distillate is richer in water; this fraction is followed by a constant-boiling mixture of benzene and alcohol, b. p. 68°, and the final fraction is dehydrated alcohol.

If the added substance is itself relatively non-volatile, the method is simplified—at least theoretically—for the distillate contains only the original constituents, being at first richer in that constituent in which the added substance is insoluble. For example, the following results were obtained by distilling (without a fractionating column) 100 c.c. of the azeotropic mixture of *n*-propyl alcohol and water (containing 28% of water) with different added substances. The first 10 c.c. of the distillate were rejected in each case, and the following 50 c.c. collected, the composition being determined by means of a refractometer.

Substance added to 100 c.c.	H_2O, %, in distillate.	Substance added to 100 c.c.	H_2O, %, in distillate.
Benzyl benzoate, 50 c.c.	30·0	Sucrose, 25 g.	21·0
Liquid paraffin, 50 c.c.	29·0	K_2CO_3, 25 g.	13·0
Palmitic acid, 50 c.c.	30·5	KOH, 25 g.	8·0
Stearic acid, 50 c.c.	31·0		

It will be noted that the water-soluble are more effective than the alcohol-soluble solutes, and that alcohol containing only 8% of water may be obtained from a single distillation with potassium hydroxide. If this distillate is fractionated, it may be separated into pure propyl alcohol and the azeotropic mixture, and the latter may be again dehydrated by distillation from the potassium hydroxide which has in the meantime been strongly heated in order to expel the water retained from the first distillation. The following results were obtained by treating 200 c.c. of the azeotropic mixture with 50 g. of potassium hydroxide in the manner indicated, the process being repeated three times : Pure propyl alcohol, 40 c.c.; 96% alcohol, 98 c.c.; 20% alcohol, 40 c.c. The process thus provides a simple method of obtaining pure propyl alcohol from the constant-boiling mixture.

Interesting temperature changes occur during the distillation of an azeotropic propyl alcohol–water mixture to which a non-volatile substance soluble in one constituent has been added. A thermometer placed in the vapour at first rises, then falls sharply for about 1°, and then again rises. For example, if a solution of stearic acid in the mixture is being distilled, the first distillate will be richer in water than the azeotropic mixture, and consequently the later distillate will be richer in alcohol. Therefore, during the transition from water-rich to alcohol-rich distillate the composition passes through that of the azeotropic mixture, *i.e.*, through a mixture of minimum b. p. This fall in the b. p. is a useful indication when to change receivers in order to separate the water-rich and the alcohol-rich fraction.

The azeotropic mixture of ethyl alcohol and water contains about 95·5% of alcohol and no solute is available which is insoluble in alcohol but soluble in water in such a mixture, so we are restricted to the use of alcohol-soluble solutes. If the mixture is distilled with an equal volume of benzyl benzoate, liquid paraffin, or stearic acid, it is possible to obtain a slightly more concentrated alcohol (*ca.* 97%) in the last portion of the distillate. More satisfactory results are obtained by combining the method with dehydration by means of lime : an equal volume of high-boiling paraffin is added to the mixture, and the whole refluxed; owing to the presence of the paraffin (which lowers the vapour pressure of the alcohol) the condensed vapour is richer in water than the original mixture, and it is allowed to percolate over a column of freshly ignited lime before returning to the boiling mixture, the process being carried out in a simple type of extraction apparatus. As it is very difficult to prevent traces of lime from entering the boiling mixture, the solute used to lower the vapour pressure of the alcohol should not be affected by the lime, so that liquid paraffin should be used instead of benzyl benzoate or stearic acid. Further, as all the water is eventually absorbed by the lime, the method should only be employed for alcohol which has already been dehydrated by distillation with potassium carbonate.

Mariller (*Compt. rend.*, **1922, 175,** 588; *Chim. et Ind.*, 1923, **10,** 643) describes the dehydration of alcohol by means of mixed dehydrating agents, potassium carbonate dissolved in glycerol being the most satisfactory. In this case, however, both constituents of the added substance lower the vapour pressure of the water relative to that of the alcohol, the solution of potassium carbonate in glycerol being a liquid with a greater affinity for water than pure glycerol. In the method now described, one constituent—the paraffin—lowers the vapour pressure of the alcohol; hence the refluxed distillate is richer in water than the original mixture and is therefore more easily acted on by the quicklime. There is thus, as it were, a " push and pull " effect applied to the water owing to the joint action of the paraffin and the quicklime.

The results obtained by the present method may be seen from the table, which compares the effects of refluxing 50 c.c. of aqueous alcohol over a column of lime for one hour, with and without the addition of an equal volume of liquid paraffin. The water content of the distillate after treatment was obtained from the refractive index of the solution as determined by means of a dipping refractometer (Leach and Lythgoe, *J. Amer. Chem. Soc.*, 1905, **27,** 964).

Composition of original mixture : EtOH, %	93·0	94·5	97·0	99·0
EtOH, %, in distillate refluxed without paraffin ...	96·0	97·7	98·7	99·5
EtOH, %, in distillate refluxed with paraffin	99·0	99·7	99·7	99·7

Finally, a sample of 50 c.c of commercial absolute alcohol (99·4%) was refluxed with paraffin over lime for 2½ hours and then distilled. The distillate contained 99·9% of alcohol, the composition being determined by means of a density measurement, as the dipping refractometer is not sufficiently sensitive to detect minute traces of water.—GLASGOW UNIVERSITY. [*Received, June 7th,* 1938.]