$$Y = A(L_1 + 5L_2) + B$$

Y = Degree of yellowing
L_1 = Linoleic acid as fraction of total
L_2 = Linolenic acid as fraction of total
A = Constant for the amber filter
B = Constant for the blue filter

Substituting the appropriate values as given in the typical fatty acid analyses of safflower and soybean oil, Table I, for soybean oil, $Y = A(.782) + B$, safflower No. 1, $Y = A(.770) + B$, safflower No. 2, $Y = A(.808) + B$, and for linseed, $Y = A(2.74) + B$. Theoretically, safflower should be as good as soya for the non-yellowing paints. Examination of the baked films after storage in a dark place for six months supports the conclusion that safflower alkyds yellow almost as much as soya resins.

TABLE VIII

Properties of Maleic Treated Oils

	Soybean Maleic Oil	Safflower Maleic Oil
Acid Number	7	8
Viscosity (100% Solids)	J	K
Color	8	8

Clocker has described the reaction of drying and semidrying oils with maleic anhydride and pentaerythritol (7). For example, soybean oil can be reacted with 3 to 7% maleic anhydride, and esterified with pentaerythritol to produce an oil which performs like linseed in drying and durability properties. This oil displays better non-yellowing properties than linseed.

To determine whether safflower will react with maleic anhydride, 200 parts of the oil were processed with 10 parts of maleic anhydride for one hour at 480°F. Pentaerythritol, technical, 6.7 parts, were added and processing continued at 520°F. for one hour. Agitation and inert gas continued throughout the entire reaction at rates previously indicated for the long oil alkyd batch. The similarity of the treated oils is evident from a study of viscosity, acid number, and color.

As with soybean maleic oils, safflower maleic oils have improved drying qualities. The oils were treated with 0.5% Pb and 0.05% Co, aged overnight, and films, .003 inch thick wet, were drawn on tin plates. Drying times were as follows:

TABLE IX

Drying Times of Maleated Oils

	Set-to-touch	6 Hours
Soya Maleic Oil	4½ hours	Heavy tack
Safflower Maleic Oil	2¾ hours	Slight tack

To generalize, safflower oil can replace soybean oil in alkyd resin formulations or maleic oils. Alcoholysis rates are usually faster with safflower oil than with soybean or linseed oils. Reaction rate curves of time versus viscosity or acid number for alkyd resin processing will be quite similar for soya and safflower oils. Although the color of the alkyd from safflower will be better than from soya, color retention of films are about equal. Safflower oil alkyds and treated oils dry considerably faster than similar soya alkyds.

The authors wish to thank Oil Seed Products Company and Petroleum Specialties for supplying samples of safflower oil.

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Correlation of Vegetable Oil-Hexane Solution Vapor Pressures

ALLEN S. SMITH, University of Notre Dame, Notre Dame, Indiana

EQUIPMENT for desolventizing vegetable oil miscellas obtained by extraction with hydrocarbon solvents has been commonly over-designed. The absence of information on the performance of packed or tray stripping columns for this purpose and of equilibrium relationships for hydrocarbon-oil solutions have contributed to evident uncertainty in design. Even with previous knowledge of plant practice and experimentally determined vapor pressure data for oil solutions the situation is not greatly improved. Such information may have been obtained with a hydrocarbon solvent of unique specifications not necessarily characteristic of all commercial solvents or all shipments from the same source.

In order to eliminate the variable of solvent composition or specifications a method has been developed by which the vapor pressure characteristics of various commercial hydrocarbon solvents, or fractions of them, in oil solutions can be obtained from known data for one hydrocarbon solvent. The result is a generalized set of data which can be used to compute vapor-liquid equilibria and enable operating conditions in desolventizing equipment to be altered to achieve optimum performance with different hydrocarbon solvents. The only information required, in addition to vapor pressure data for one solvent-oil system, is the normal bubble point of the solvent or solvent fraction. The method is developed in this paper and justified by the use of experimental vapor pressure data on commercial hexane and heptane solutions of soybean oil.

Viscosity, density, heat of solution *(3)*, and vapor pressure data *(8)* indicate that solutions of hexane and soybean oil are not normal or ideal solutions. The actual pressure of hexane over soybean oil solutions is less than that calculated for an ideal solution; i.e., $p/PX < 1$ where p is the pressure over the solution, P is the vapor pressure of the pure solvent, and X is concentration. The difference, described as a negative deviation from ideal solution, is assumed

TABLE I

Characteristics of Commercial Hexanes

Solvent	Phillips		Ansco		Skellysolve B	
	Temp. °F. at 760 mm.	Pressure at 230°F.	Temp. °F. at 760 mm.	Pressure at 230°F.	Temp. °F. at 760 mm.	Pressure at 230°F.
A. S. T. M. Distillation[a]						
I. B. P.	151	2532 mm.	153	2459 mm.	140	2971 mm.
50%	153	2459	156	2351	......	....
90%	155	2388	157	2318	......	....
Dry point	156	2351	158	2283	160	2217
Variation in pressure from I.B.P., %	......	7.2	......	7.2	......	25.4
Temperature to give pressure at dry point equal to pressure at I. B. P	......	243.7°F.	......	243.3°F.	......	286.8°F.

[a] Taken from manufacturers' bulletins.

to be a characteristic of the oil, and not of hexane in the solution. If this is true, then the escaping tendency, or chemical potential, of hexane from soybean oil solution will be equal to that of other saturated hydrocarbons at the same temperature and molar concentration. For two hydrocarbons then, such as heptane and hexane, $p_1/P_1 = p_2/P_2$ *and* $p_1 = p_2 P_1/P_2$. The conclusion follows that the pressure of heptane over a solution of oil is equal to that of hexane from the same molar concentration of the oil multiplied by the ratio of the vapor pressures of the pure solvents at the same temperature.

The significance of this conclusion lies in the possibility of obtaining vapor pressure data of oil solutions of commercial hydrocarbon solvents, or fractions of them, from experimental data with one solvent of the same type. Data which have been published *(4, 8)* are characteristic of a particular commercial hexane. Other hexanes will exhibit similar deviations but different pressures from oil solutions at equal temperatures, and new data would be required for each solvent in the absence of a correlation. However data on a whole commercial hexane are of little value practically, inasmuch as the hexane is fractionated during evaporation from miscella. The fraction remaining in the oil and requiring vacuum steam stripping is a relative high boiling portion of the whole solvent. Specific data are required for this hexane fraction for rational design and operation. The magnitude of the differences between several commercial hexanes and their fractions is shown in Table I. A temperature of 230°F. has been assumed for a solvent stripping operation of the various fractions from an oil. The last line in the Table indicates the temperature at which the stripper would give the same performance, other factors being constant, when the solvent content of the oil approaches zero. If the operating temperature is fixed, then other factors as pressure or steam rate must be changed to achieve equal performance. Consequently, for optimum performance of the equipment and efficiency of operation, design and operation of equipment should be based on the vapor pressure characteristics of a particular fraction of the commercial hexane used.

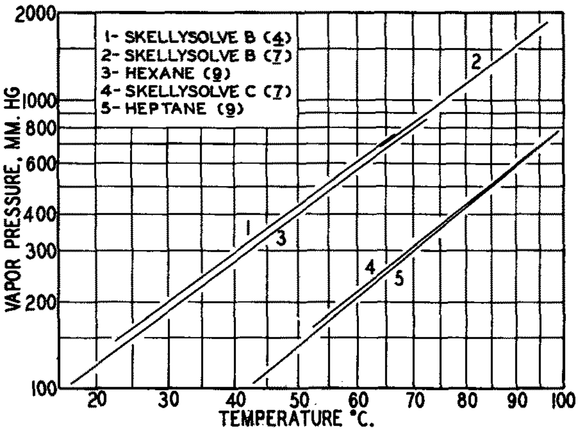

FIG. 1. Vapor pressures of pure and commercial hydrocarbon solvents.

Vapor Pressure of Paraffin Hydrocarbons

The application of the equation $p_1 = p_2 P_1/P_2$ requires a means of obtaining the vapor pressures P_1 and P_2 of the pure reference solvent and of the solvent or solvent fraction of interest at the temperature of operation. The following method has been convenient.

The vapor pressure of the normal paraffin hydrocarbons can be represented as a linear function of temperature on a Cox-type chart *(5)*. The equation relating the variables is the Antoine equation: $\log_{10}P = A - B/(t+C)$ in which A, B, and C are constants. A satisfactory value for C is 230 when t is in °C. *(2)*. Data for a series of hydrocarbons form a family of straight lines which intersect at a common point with the coordinates t_∞ and P_∞. From this common point of intersection and the normal boiling or bubble point for a hydrocarbon or mixture of hydrocarbons of the same series, the complete vapor pressure-temperature relation can be established.

A Cox-type chart is shown in Figure 1 for n-hexane, n-heptane, and several commercial hydrocarbon solvents. The common point of intersection for the aliphatic hydrocarbon series has the coordinates $P_\infty = 1.3 \times 10^6$ mm. and $t_\infty = 1240$°C. *(1)*. This point and the normal bubble point of the commercial solvents have been used to compute the A and B constants in the equations representing the lines. Values of the constants, calculated by the following equations *(2)*, and data from which they were obtained are given in Table II.

TABLE II

Constants in Vapor Pressure Equation for Various Solvents

Solvent	Bubble Point, °C.	Pressure, mm.	*A*	*B*
n-Hexane *(9)*	68.74	760	6.9385	1212.1
	75	921.3	....	....
	100	1842.5	....	....
	125	3342.7	....	....
Eastman, No. 1 *(8)*	68.5	740	6.9406	1215.3
Eastman, No. 2 *(6)*	67.3	742	6.9361	1208.8
Skellysolve B, No. 1 *(7)*	67.2	740	6.9361	1208.7
Skellysolve B, No. 2 *(4)*	66.0	740	6.9339	1202.6
Skellysolve C *(7)*	83.2	489.3	7.0411	1362.9
n-Heptane *(9)*	98.4	760	7.0441	1367.3

$$B = (t_B + 230)(t_\infty + 230)(\log_{10}[P_\infty/P_B])/(t_\infty - t_B)$$

$$A = \log_{10}P_\infty + B/(t_\infty + 230)$$

TABLE III

Vapor Pressures of Soybean Oil Solutions *(7)*
Skellysolve B, No. 1
Temperature °F.

171.0			216.1			253.3		
Solvent		*P* mm.	Solvent		*P* mm.	Solvent		*P* mm.
Wt. %	Mol. Frac.	Hg	Wt. %	Mol. Frac.	Hg	Wt. %	Mol. Frac.	Hg
0.41	0.04	29	0.85	0.08	100	0.30	0.03	64
0.85	0.08	51	1.20	0.11	128	0.96	0.09	156
1.97	0.17	101	1.84	0.16	181	1.08	0.10	175
2.37	0.20	125	2.11	0.18	200	1.32	0.12	207
2.52	0.21	133	2.37	0.20	227	1.35	0.12	216
3.18	0.25	156	3.51	0.27	300	1.44	0.13	226
4.43	0.32	206	4.43	0.32	368	1.84	0.16	282
5.25	0.36	240	4.43	0.32	369	2.23	0.19	316
5.81	0.39	256	5.58	0.38	438	3.68	0.28	494
8.00	0.47	321	5.86	0.39	460	5.25	0.36	632
9.05	0.50	359	6.90	0.43	523	......	......	......
......	......	......	7.34	0.45	554	......	......	......

Skellysolve C
Temperature, °F.

Solvent		149.7	174.9	199.9	225.0	251.0
Wt. %	Mol. Frac.	Pressure, mm. Hg absolute				
2.16	0.16	25	38	57	81	114
5.21	0.32	57	86	127	187	268
10.1	0.5	94	149	227	336	475
100	1.0	270	430	670	1000	1485

P_B is the vapor pressure in mm. at temperature t_B in °C.

The use of the common point of intersection for the aliphatic hydrocarbon series to compute data for the commercial solvents is correct only if no olefinic, naphthenic, or aromatic hydrocarbons are present. Although experimental data for the three commercial hydrocarbon solvents can be represented by the Antoine-type equation used, as shown in Figure 1, no common point of intersection necessarily exists. The application of the method of obtaining a vapor pressure-temperature relation to the commercial solvents has been made with the assumption that their non-aliphatic content is small and that any error is consequently small over the limited temperature range of interest in solvent recovery. Thus the difference between calculated and smoothed experimental vapor pressures for the Skellysolve B represented by curve 1 in Figure 1 is zero over the experimental temperature range.

Vapor Pressure Correlation for Soybean Oil Solutions

Data for commercial hexane-soybean oil solutions covering a temperature range of 167° to 257°F., a concentration range from 0 to 39.5 weight percentage solvent, and a pressure range from 0 to 744 mm. have been used in the correlation. The solvents were Skellysolve B, designated as No. 1 in Table II, *(7)* and Eastman practical hexane which has been designated as samples No. 1 *(8)* and No. 2 *(6)*. A single investigation *(7)* of commercial heptane-soybean oil solutions has been used in justifying the correlation. Experimental data with this solvent (a Skellysolve C) and with Skellysolve B have not been published and are given in Table III.

These four sets of data, independently determined by four different methods, shown in Figure 2, have been referred to n-hexane in the final correlation. This was accomplished by use of the equation $p_1 = p_2 P_1/P_2$. p_2 is the experimentally determined vapor pressure of a solution. P_2 and P_1, the vapor pressures of pure solvent and of n-hexane at the same temperature as p_2, were evaluated from the data in Table II by the method previously described. Figure 2 shows p_1, the pressure of n-hexane solutions of soybean oil, as a function of concentration at constant temperature and represents the data with the four different solvents. Interpolation and extrapolation of the latter data to the three temperatures of 167°, 212°, and 257°F., necessary for three of the investigations, was accomplished by plotting vapor pressures of solutions against temperature on a Cox-type chart at constant composition. This method has been shown to give linear relationships of the variables *(8)*. Interpolation between the isotherms in Figure 2 for practical use is more readily accomplished at high solvent con-

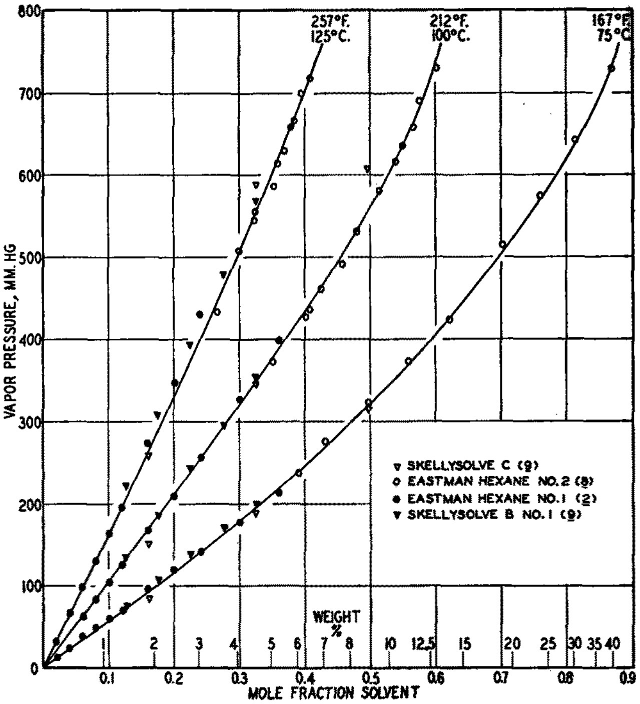

FIG. 2. Correlation of vapor pressure data for hydrocarbon solvent-soybean oil solutions referred to n-hexane.

centrations by plotting temperature against concentration at constant pressure. This is illustrated in Figure 3.

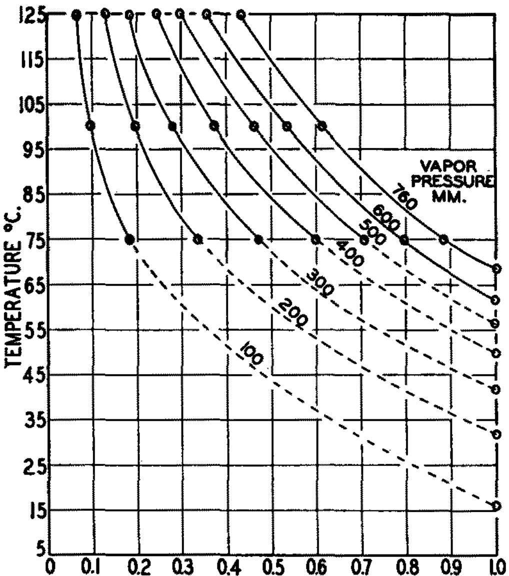

FIG. 3. Temperature interpolation plot for hydrocarbon solvent-soybean oil solution vapor pressure data referred to n-hexane.

The unit of concentration which is necessarily used in this correlation is the mole fraction. A molecular weight of 876 has been used for soybean oil. The molecular weights of n-hexane and n-heptane have been used for the commercial solvents as spreads of 5° to 10°F. in their boiling ranges do not change the molecular weight appreciably.

Application

The following example is given to illustrate the use of the correlation and the magnitude of the differences between solvents. Assume that the solvent content of a miscella is to be reduced to 8.95 wt. % or 0.5 mol. fraction at 212°F. A comparison will be made of the actual concentration obtained when three solvents or solvent fractions boiling 5°F. apart are used. The necessary information, given in Table IV, is obtained by the following procedure.

TABLE IV

Effect of Solvent Boiling Point on Vapor Pressure of a 0.5 Mole Fraction Hexane-Oil Solution

Solvent B.P. at 760 mm., °F.	150	155	160
A from Equation (2).....................	6.9277	6.9372	6.9467
B from Equation (3).....................	1196.1	1210.1	1224.1
P_1 from Equation (1) at 100°C.....	2010	1862	1727
P_2 of n-hexane at 100°C. = 1842 mm..................................	......	......	......
p_2 of n-hexane from 0.5 mol. frac. solution = 560 from Fig. 2........	......	......	......
p_1 from Equation (4).....................	610	566	525

Calculate the vapor pressure P_1 of the solvent at 212°F.(100°C.) by equation (1). The constants A and B are obtained as previously described or, more conveniently for hexane fractions, from equations (2) and (3). P_2, the vapor pressure of n-hexane, is given in Table II and may be evaluated at other temperatures by equation (1) with the constants given in Table II. Read p_2 from Figure 2, which gives the vapor pressure of n-hexane from a 0.5 mole fraction solution at 100°C. Calculate p_1, the vapor pressure of the solvent considered from the same solution, by equation (4).

$$\log P = A - B/(t + 230) \tag{1}$$

in which t is the operating temperature in °C.

$$A = 0.0019\ T + 6.6427 \tag{2}$$

$$B = 2.8\ T + 776.1 \tag{3}$$

in which T is the normal boiling point of the solvent in °F.

$$p_1 = p_2 P_1 / P_2 \tag{4}$$

The tabulated calculations indicate that a variation of ± 5°F. in the normal boiling point of the solvent causes a difference of ± 7.5% in the vapor pressure of the solvent from solution. Reference to Figure 2 shows that this pressure change is equivalent to a concentration change of ± 6%. An increase of 8°F. in operating temperature, other conditions being constant, would correct for the increase in residual solvent left in an oil by use of a solvent boiling 5°F. higher than one for which the equipment was designed. The percentage changes remain the same at lower solvent concentrations where the actual concentrations are of greater significance.

Summary

Variations between commercial hexanes from different sources and boiling ranges of some solvents are sufficiently large to require specific data on vapor pressures for the solvent or solvent fraction in a miscella. Pressure-concentration-temperature relations, experimentally determined for three commercial hexanes and a heptane in soybean oil, have been correlated and presented graphically as a single set of curves, characteristic of n-hexane. An example of a method is given by which these curves can be used to obtain specific data for any hexane solvent. A variation of ± 5°F. in solvent boiling point is shown to cause a ± 6% change in miscella concentration which can be corrected by a change of ± 8°F. in operating temperature. This effect is due to a ± 7.5% variation in miscella vapor pressure, when the solvent boiling point varies by ± 5°F., which is sufficiently greater than the uncertainty of pressures read from the correlation, about ± 2%, to require consideration in design and operation of solvent recovery equipment.

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