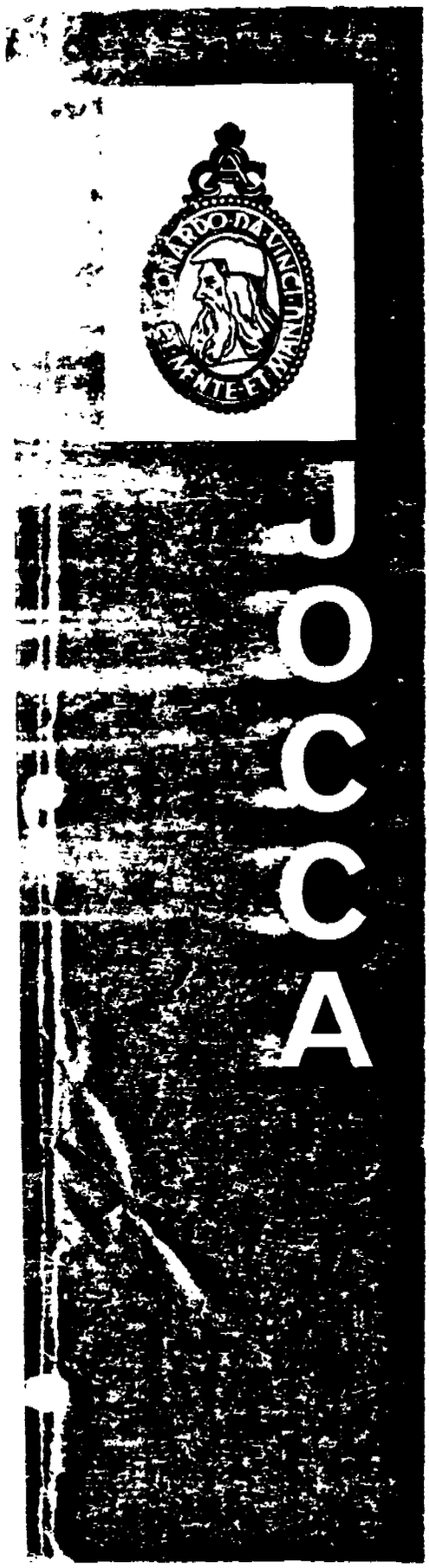
V I. 60 No. 7 JOCCAB 60(7) 245-274 (1977) July 1977



JOURNAL OF THE OIL & COLOUR CHEMISTS' ASSOCIATION

OCCA-30 EXHIBITION INVITATIONS TO EXHIBIT DESPATCHED

Details on page 270

same vinyl chloride copolymer mentioned above[5]. Polymers with lower glass transition temperatures can be expected to retain less solvent (or monomer) because of greater internal mobility. Poly(vinyl chloride) (PVCl) is generally plasticised or modified by copolymerisation to allow its use in a solution coating. Such coatings can be expected to retain less solvent or monomer than rigid poly(vinyl chloride), for example.

It might also be noted that the mathematics of diffusion predict a dependence of solvent loss on the square of the film thickness. This means that if a drying film is compared with one of twice its film thickness (at longer times), the thicker film will require four times as long to reach the same level of solvent (or monomer) content as the thinner film. Thus thicker films can inherently be expected to retain more solvent or monomer than thinner films. These relations have also been confirmed experimently in the experiments mentioned above.

Estimates of vinyl chloride loss during the first phase

Refs. 3, 5-7

The first phase evaporation phenomena are closely related to what in the chemical engineering literature is termed "differential distillation" (distilling solvents in a batch process, for example). The polymer may influence the process to some degree, as will the activity coefficients for the mixtures involved. In a first approximation, however, these will not be considered.

The differential distillation process is described by McCabe and Smith[6]. In the simplest case, mathematical relations are derived for estimating the compositional changes in the liquid film as a function of material evaporated.

The equation concerned is:

$$\left(\frac{N_B}{N_{Bo}}\right) = \left(\frac{N_A}{N_{Ao}}\right)^{\alpha_{BA}} \quad \ldots\ldots\ldots\ldots (1)$$

where:

N_B = amount of B(VCM) present at a given stage in the evaporation process

N_{Bo} = amount of B originally present

N_A = amount of A present at a given stage in the evaporation process

N_{Ao} = amount of A originally present

α_{BA} = relative volatility of B to A

The relative volatility can be estimated by a simple ratio of the evaporation rates, but this value is not available for vinyl chloride. In the example below the relative volatility was, therefore, estimated by a ratio of the vapour pressures at room temperature[6,7].

$$\alpha_{BA} \approx \left(\frac{P_B}{P_A}\right) \quad \ldots\ldots\ldots\ldots (2)$$

Example:

Assuming a typical lacquer formulation having the following composition:

Vinyl copolymer 25g

Methyl ethyl ketone 75g

Vinyl chloride monomer variable

The above mentioned experiments with VYHH have demonstrated that the end of the first phase is associated with a solvent composition of about 0.2g solvent/g VYHH[5]. Thus, the first phase represents a reduction of the volatile content of the lacquer from 3g/g VYHH to 1/15 of this value before entering into the second phase. α_{BA} at 20°C is approximately 2650/71.5 = 37.06 from equation 2.

Substituting these values into equation 1 gives:

$$\frac{N_{VCM}}{N_{VCMo}} = \left(\frac{1}{15}\right)^{37.06} = 2.59 \times 10^{-44}$$

Thus it is clear that theoretically there should be essentially no VCM remaining at the end of the first stage of the evaporation process.

For the sake of including all factors, the data on solvent retention for VYHH cited above indicate that a further reduction of the solvent and/or monomer content present at the start of the diffusion controlled phase will occur to the extent of a factor somewhat greater than two within a reasonable time (hours). Should the temperature be increased above room temperature, the mobility of the polymer chain segments will be increased with an accompanying increase in the diffusion coefficients of the solvent/monomer molecules. A greater reduction in the amount of retained volatile material will result.

Experimental

Refs. 8-11

The analyses for VCM were carried out using a gas chromatograph. For liquid samples with a large VCM content the solvent or lacquer solution was injected directly into the gas chromatograph. When the VCM content was small, the analysis was done by the head space method[8-11]. Here the principle is to place the sample in a suitable container, such that a gaseous sample can be removed with a syringe through a membrane without otherwise disturbing the contents. The volatile contents establish an equilibrium in the container and a calibration of the VCM signal by the method of addition allows analysis of the VCM content in the sample itself.

Experimental results—films

A commercially available lacquer with the composition described in the example above was used for these studies. This lacquer was found to have 16ppm VCM based on the nonvolatile portion of the formulation. Films were made in Petri dishes. These were made at an exaggerated film thicknesses of 140 to 180 microns. After 66 hours of drying at room temperature (according to the film thickness squared rule this corresponds to 1.6 minutes for the normal film thickness of 3 microns for this product) no measurable (< 1ppm) VCM could be detected in the film.

It might also be noted that measurable VCM could not be found in films applied in the manner the product is customarily used ie in a film thickness of 3 microns on aluminium foil.

Experimental results—evaporation

Experimental values for α_{BA} were determined by adding 4000ppm VCM to methyl ethyl ketone (MEK) and following the concentration of VCM as a function of the per cent MEK evaporated. Figure 1 shows a gas chromatogram of the VCM/MEK mixture after 4 per cent MEK and 48 per cent VCM are evaporated. Collected results from similar analyses are shown in Figure 2.

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DEPARTMENT OF THE INTERIOR

(BUREAU OF RECLAMATION)

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VR 3

VINYL RESIN PAINT: Aug 14, 1964 UNION CARBIDE Formulation VP-3010 using BAKELITE vinyl resins VMCH and VYHH.

FORMULA SUGGESTION VP-3010

Maintenance Primer Finish*

FORMULA	Parts by Weight
BAKELITE Vinyl Resin VMCH	11.1
BAKELITE Vinyl Resin VYHH	4.5
FLEXOL Plasticizer DOP	3.0
Pigment (1)	13.0
Asbestine 3X	3.9
Methyl Isobutyl Ketone	16.1
2 Nitropropane	16.2
Toluene	32.2
	100.0

(1) White System – Titanium Dioxide, rutile, non-chalking.
Red System – Synthetic Red Iron Oxide.
Black System – Synthetic Black Iron Oxide.
Aluminum System – Aluminum Powder, 9.9 parts rather than 13.0 parts.

PROCEDURE

1. Dissolve resins into the solvent system.
2. Charge all ingredients** and resin solution into pebble mill and grind for 24 hours.

**except in aluminum system

*For best adhesion of primers to bare steel, it is helpful to add ¼% of 85% phosphoric acid, based on the weight of vinyl resin VMCH, to the primer formulation.

VR-6

VINYL RESIN PAINT: July 6 1960 UNION CARBIDE Formulation VP-3001 using BAKELITE vinyl resins VMCH in prime coat, VYHH in body coat and VYHH and VYNS in seal coat.

FORMULA SUGGESTION VP-3001

Maintenance System

	Parts by Weight			
FORMULA	Prime* Coat	Red Body Coat	Grey Body Coat	Seal Coat
BAKELITE Vinyl Resin VMCH	15.00	–	–	–
BAKELITE Vinyl Resin VYHH	–	15.00	15.00	13.47
BAKELITE Vinyl Resin VYNS	–	–	–	5.77
FLEXOL Plasticizer 10-10	3.00	3.00	3.00	1.38
TiO_2, rutile, non-chalking	15.00	–	15.00	–
Carbon Black	1.00	–	1.00	–
Synthetic Red Iron Oxide	–	15.00	–	–
Aluminum Powder (1)	–	–	–	(1)
Methyl Isobutyl Ketone	16.50	17.00	16.50	19.85
2 Nitropropane	16.50	17.00	16.50	19.84
Toluene	33.00	33.00	33.00	39.69
	100.00	100.00	100.00	100.00

(1) "Alcoa" 408 suggested – 1.5 lbs to be added to 1 gallon of solution for use.

*For best adhesion of primers to bare steel, it is helpful to add ¼% of 85% phosphoric acid, based on the weight of vinyl resin VMCH, to the primer formulation.

PROCEDURE

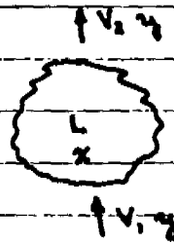
1. Dissolve resins in solvent system.
2. Charge all ingredients** and resin solution to pebble mill and grind for 24 hours.

**except in aluminum system

Derivation of Equations

BATCH STRIPPING OR DRYING

Consider a quantity of liquid, L lb-moles. Vapor is passed over this liquid at a rate, V lb-moles/hr. As it does so, some of the liquid evaporates, and is carried off with the vapor, so that the vapor leaving, V_2 lb-moles/hr, is greater than the incoming vapor and the amount of liquid has been reduced.



Over a small amount of time, $d\theta$, write material balances:

(1) Overall · $V_2 d\theta = V d\theta - dL$

(2) Any component · $V_2 y d\theta = V y_0 d\theta - d(Lx)$

(Note that dL and $d(Lx)$ are negative because L and Lx are decreasing as time increases)

Solving (1) for V_2 and substituting into (2)

(3) $$V(y - y_0) = y\frac{dL}{d\theta} - \frac{d(Lx)}{d\theta}$$

Expanding $d(Lx)$ to $x\,dL + L\,dx$ gives

(4) $$V(y - y_0) = (y - x)\frac{dL}{d\theta} - L\frac{dx}{d\theta}$$

Assume heat transfer is sufficient to maintain a constant evaporation rate, $R \equiv -dL/d\theta$. Then

(5) $$d\theta = -dL/R,$$

which can be substituted into (4) to give

(6) $$\frac{V}{R}(y - y_0) + (y - x) = L\frac{dx}{dL}$$

or

(7) $$\frac{dL}{L} = \frac{dx}{y\left(\frac{V}{R}+1\right) - \frac{V}{R}y_0 - x}$$

Integrating

(8) $$\ln \frac{L_1}{L_2} = \int_{x_2}^{x_1} \frac{dx}{y\left(\frac{V}{R}+1\right) - \frac{V}{R}y_0 - x}$$

In the drying of the PVC resin, $y_0 = 0$. If we assume that y and x are in equilibrium, $y = \frac{\gamma P}{\pi} x$, where γ is the activity coefficient, P is the pure component vapor pressure, and π is the total pressure. Alternately, we can assume an efficiency, E, which we will define as $y/\left(\frac{\gamma P x}{\pi}\right)$. Making these substitutions

(9) $$\ln \frac{L_1}{L_2} = \int_{x_2}^{x_1} \frac{1}{\frac{E\gamma P}{\pi}\left(\frac{V}{R}+1\right) - 1} \frac{dx}{x}$$

If we assume E, γ, P, π, V, R are constant (or a good average value can be used), the following equation results

(10) $$\ln \frac{x_1}{x_2} = \left[\frac{E\gamma P}{\pi}\left(\frac{V}{R}+1\right) - 1\right] \ln \frac{L_1}{L_2}$$

To use this equation, one must know initial and final quantities of liquid, the initial composition, the vapor rate, the evaporation rate, and the temperature (in order to know vapor pressures). The efficiency is determined so that Σx_2 for all components = 1.0.

B. Y. Hill

2/22/78

ACTIVITY COEFFICIENTS OF SOLVENT COMPONENTS IN PVC 'VARNISH'

We shall assume that the primary cause of activity coefficient's being different from 1.0 in the varnish is the large size of PVC resin molecules. This size effect is best treated by the Flory-Huggins equation:

$$(1) \qquad \frac{\Delta G_{mix}}{RT} = \sum_{k=1}^{N} n_k \ln \Phi_k + \left[\sum_{\substack{k=1 \\ k\neq p}}^{N} n_k + m n_p\right]\left[\sum_{k=1}^{N-1}\sum_{j=k+1}^{N} \Phi_k \Phi_j \chi_{kj}\right]$$

where Φ_k = approximate volume fraction of component k

$$\Phi_k = \frac{n_k}{\sum_{\substack{i=1 \\ i\neq p}}^{N} n_i + m n_p} \qquad \text{for } k \neq p$$

and

$$\Phi_p = \frac{m n_p}{\sum_{\substack{i=1 \\ i\neq p}}^{N} n_i + m n_p}$$

n_k = no. of moles of component k in liquid

m = ratio of size of resin (or polymer) molecule to that of solvent molecules. This treatment neglects size differences between the various solvent molecules.

χ_{kj} = empirical interaction term to reflect enthalpy of mixing of components k and j.

N = total number of components

subscript p refers to resin.

ΔG_{mix} = free energy of mixing

We have chosen to neglect the enthalpy of mixing, since the bulk of the solvent is toluene and xylene and we would expect a low enthalpy of mixing. Also, we would expect our components to deviate positively from ideality

yielding higher activity coefficients than would be predicted if this term is neglected. Thus, for our primary interest, vinyl chloride, which is very dilute in our system, we will obtain an value of γ, the activity coefficient, that is low, and will be conservative in predicting the residual vinyl chloride in the resin. Therefore, we set all $\chi_{k,j}$'s = 0, giving

$$(2) \qquad \frac{\Delta G_{mix}}{RT} = \sum_{k=1}^{N} n_k \ln \Phi_k$$

(Equation 1 is derived similarly to that used for the multicomponen Scatchard-Hildebrand equation, as outlined in Prausnitz, Molecular Thermodynamics of Fluid Phase Equilibria, pp 218-9.)

From classical thermodynamics

$$(3) \qquad \ln \gamma_i = \frac{\bar{g}_{ei}}{RT} = \frac{\bar{g}_{mix,i}}{RT} - \left(\frac{\bar{g}_{mix,i}}{RT}\right)_{ideal}$$

$$(4) \qquad \left(\frac{\bar{g}_{mix}}{RT}\right)_{ideal} = \ln x_i$$

$$(5) \qquad \frac{\bar{g}_{mn,i}}{RT} = \partial\left(\frac{\Delta G_{mix}}{RT}\right)\Big/\partial n_i$$

where γ_i is the activity coefficient of component i, relative to Raoult's Law, $\bar{g}_{ei}$ is the partial molal excess free energy of component i, $\bar{g}_{mix,i}$ is the partial molal free energy of component i in the real mixture, $\bar{g}_{mix,i,ideal}$ is the partial molal free energy that i would have in an ideal mixture, and x_i is the mole fraction of component i. R is the gas constant and T is the absolute temperature.

Differentiating equation (2) with respect to n_i, after substituting the definition of Φ_k:

$$(6)\quad \frac{\partial(\Delta G_{mix}/RT)}{\partial n_i} = \frac{\partial}{\partial n_i}\left[\sum_{\substack{k=1\\k\neq p}}^{N} n_k \ln\left(\frac{n_k}{\sum_{\substack{j=1\\j\neq p}} n_j + mn_p}\right) + n_p \ln\frac{mn_p}{\sum_{\substack{j=1\\j\neq p}} n_j + mn_p}\right]$$

$$= \sum_{\substack{k=1\\k\neq p\\k\neq i}}^{N} n_k \left(\frac{\sum_{j\neq p}^{N} n_j + mn_p}{n_k}\right)\left(-\frac{n_k}{\left[\sum_{j\neq p} n_j + mn_p\right]^2}\right)$$

$$+ n_p \left(\frac{\sum_{j\neq p} n_j + mn_p}{mn_p}\right)\left(-\frac{mn_p}{\left[\sum_{j\neq p} n_j + mn_p\right]^2}\right)$$

$$+ \ln\frac{n_i}{\sum_{j\neq p} n_j + mn_p} + n_i\left[\frac{\sum_{j\neq p} n_j + mn_p}{n_i}\right]\left[\frac{1}{\sum_{j\neq p} n_j + mn_p} - \frac{n_i}{\left(\sum_{j\neq p} n_j + mn_p\right)^2}\right]$$

$$(7)\quad \frac{\bar{g}_{mix,i}}{RT} = 1 + \sum_{\substack{k\neq p\\k\neq i}}^{N} -\frac{n_k}{\sum_{j\neq p} n_j + mn_p} - \frac{n_i}{\sum_{j\neq p} n_j + mn_p} - \frac{n_p}{\sum_{j\neq p} n_j + mn_p} + \ln\frac{n_i}{\sum_{j\neq p} n_j + mn_p}$$

$$= 1 - \sum_{\substack{k\neq p\\k\neq i}}^{N} \Phi_k - \Phi_i - \frac{1}{m}\Phi_p + \ln\Phi_i$$

since $\sum_{\text{all } k}^{N} \Phi_k = 1.0$

$$(8)\quad \frac{\bar{g}_{mix,i}}{RT} = 1 + \Phi_p - \sum_{\text{all } k} \Phi_k - \frac{1}{m}\Phi_p + \ln\Phi_i$$

$$= \left(1 - \frac{1}{m}\right)\Phi_p + \ln\Phi_i$$

or

$$(9)\quad \frac{\bar{g}_{ei}}{RT} = \left(1 - \frac{1}{m}\right)\Phi_p + \ln\Phi_i - \ln x_i$$

$$= \left(1 - \frac{1}{m}\right)\Phi_p + \ln\left(\Phi_i/x_i\right)$$

(10) $$\ln(\Phi_i/x_i) = \frac{n_i}{\sum_{j\neq p} n_j + m n_p} \cdot \frac{\sum n_k}{n_i}$$

$$= \sum_{j\neq p} \Phi_j \pm \frac{1}{m}\Phi_p$$

$$= \sum_{all\ j} \Phi_j = \Phi_p + \frac{1}{m}\Phi_p = 1 - \Phi_p\left(1-\frac{1}{m}\right)$$

Therefore

(11) $$\ln \gamma_i = \frac{\overline{g^E_i}}{RT} = \Phi_p\left(1-\frac{1}{m}\right) + \ln\left(1-\Phi_p\left(1-\frac{1}{m}\right)\right)$$

Note that the activity coefficient depends only on the relative size of the resin molecule, and on its 'volume' fraction. Thus, all of the solvent components have the same activity coefficient, given by equation (11).

B. Y. Hill

Feb. 23, 1978

BATCH DRYING EQUATION WITH γ VARYING VIA FLORY-HUGGINS EQN

Before integrating, the differential equation for batch drying is

(1) $$\frac{dx}{x} = \left[\frac{E\gamma P}{\pi}\left(\frac{V}{R}+1\right) - 1\right]\frac{dL}{L}$$

From Flory-Huggins

(2) $$\ln\gamma = \Phi_p\left(1-\frac{1}{m}\right) + \ln\left(1-\Phi_p\left(1-\frac{1}{m}\right)\right)$$

which can be rewritten

(3) $$\gamma = \left(1-\Phi_p\left(1-\frac{1}{m}\right)\right)\exp\left(\Phi_p\left(1-\frac{1}{m}\right)\right)$$

At any time, the moles of liquid, $L = \sum n$ (all components). The volume fraction of resin, Φ_p is

(4) $$\Phi_p = \frac{mn_p}{\sum_{j\neq p} n_j + mn_p} = \frac{mn_p}{\sum_{all} n + (m-1)n_p} = \frac{mn_p}{L+(m-1)n_p}$$

and

(5) $$\Phi_p\left(1-\frac{1}{m}\right) = \frac{(m-1)n_p}{L+(m-1)n_p}$$

Next we substitute (5) into (2), and the result into (1). However, it is convenient to define

(6) $$K = \frac{EP}{\pi}\left(\frac{V}{R}+1\right) = \text{constant}$$

(7) $$b = (m-1)n_p = \text{constant}$$

(since the resin does not evaporate, n_p does not change)

(8) $$z = \frac{b}{L+b} = \Phi_p\left(1-\frac{1}{m}\right), \text{ variable}$$

Rearranging (8) gives

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(9) $$L = b\left(\frac{1}{z} - 1\right)$$

(10) $$dL = -b/z^2\, dz$$

(11) $$\frac{dL}{L} = \frac{dz}{z(z-1)}$$

Now the substitutions

(12) $$\frac{dx}{x} = \left[K(1-z)e^z - 1\right]\frac{dz}{z(z-1)}$$

(13) $$\frac{dx}{x} = -\frac{dz}{z(z-1)} - K\frac{e^z dz}{z}$$

(14) $$\frac{dx}{x} = \frac{dz}{z} - \frac{dz}{z-1} - K\frac{e^z dz}{z}$$

(15) $$\ln\frac{x_1}{x_2} = \ln\frac{z_1}{z_2} - \ln\frac{z_1-1}{z_2-1} - K\int_{z_2}^{z_1}\frac{e^z dz}{z}$$

(16) $$\ln\frac{x_1}{x_2} = \ln\frac{z_1}{z_2} - \ln\frac{z_1-1}{z_2-1} - K\ln\frac{z_1}{z_2} - K\sum_{n=1}^{\infty}\frac{z_1^n - z_2^n}{n\cdot n!}$$

(17) $$\ln\frac{x_1}{x_2} = K\left[\ln\frac{z_2}{z_1} + \sum_{n=1}^{\infty}\frac{z_2^n - z_1^n}{n\cdot n!}\right] - \ln\frac{z_2(z_1-1)}{z_1(z_2-1)}$$

This compares with

(18) $$\ln\frac{x_1}{x_2} = \left(K\bar{z} - 1\right)\ln\frac{L_1}{L_2}$$

for the constant γ model. But

(19) $$L_1/L_2 = \frac{z_2(1-z_1)}{z_1(1-z_2)}$$

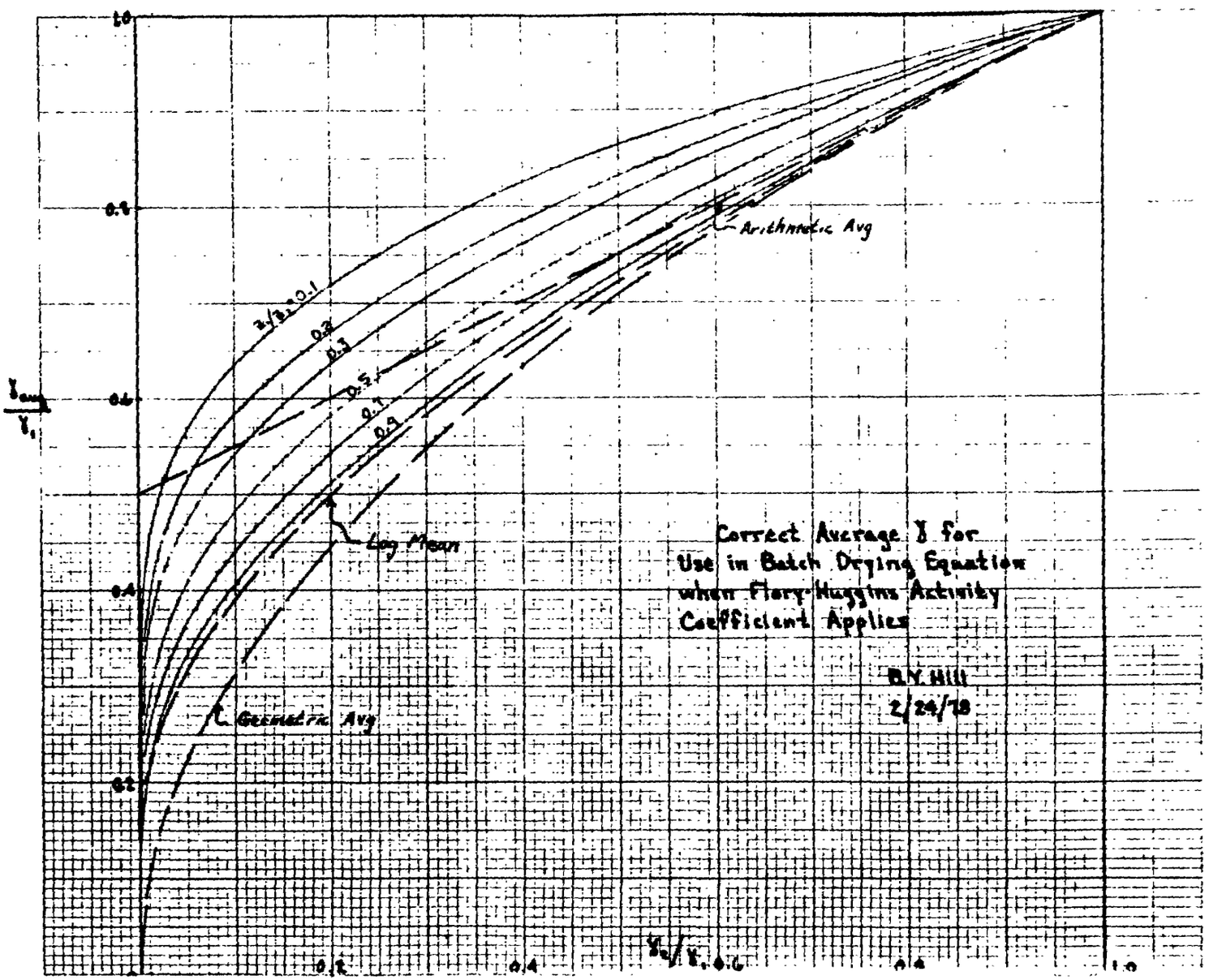
Equating (17) and (18) gives

(20) $$\gamma_{mean} = \frac{\ln z_2/z_1 + \sum_{n=1}^{\infty}\frac{z_2^n - z_1^n}{n\cdot n!}}{\ln\left(\frac{z_2}{z_1}\cdot\frac{(1-z_1)}{(1-z_2)}\right)}$$

One can readily see that this is not one of the commonly used averages, and that the proper average γ is a function of z_1/z_2. The formula is cumbersome to use since it includes a series. The attached graph is a plot of the proper (γ_{avg}/γ_1) vs (γ_2/γ_1) with z_1/z_2 as parameter. $[z_1/z_2 = \Phi_{P1}/\Phi_{P2}]$. Subscripts 1 and 2 refer to initial and final conditions respectively.

B. Y Hill

Feb. 24, 1978


1.0
0.8
0.6
0.4
0.2
0.2
0.4
0.6
0.8
1.0
$\frac{\gamma_{avg}}{\gamma_1}$
x_2/x_1
$x_2/x_1=0.1$
0.2
0.3
0.5
0.7
0.9
Arithmetic Avg
Log Mean
Geometric Avg
Correct Average γ for
Use in Batch Drying Equation
when Flory-Huggins Activity
Coefficient Applies
B.Y. Hill
2/24/78

APPENDIX II

CALCULATION OF δ_{SOLV}, STEP (1)

Activity Coefficiet of Solvent in Varnish - Step (1)

① Calculate Φ_{P_1} / Φ_{P_2} ($= Z_1/Z_2$, B.Y. Hill memo nomenclature)

$$\Phi_P = \frac{m n_P}{n_{solv} + m n_P}$$

where, n_P = moles of resin (constant)
n_{solv} = total moles of solvent
$m = \frac{V_P}{V_{solv}}$ = ratio of molar volumes of resin to solvent.

where, $V = \frac{\text{Molecular weight}}{\text{Specific Gravity}}$

a) Calculate Φ_{P_1} at beginning of step (1)

Solvent properties:

Component	MW	Sp Gr	lb	w.f.	mol	m.f.
Acetone	58.1	.7917	.1300	.100	.0022	.147
MEK	72.1	.8061	.1937	.149	.0027	.177
Toluene	92.1	.8684	.7358	.566	.0080	.527
Xylene	106.1	.8698	.2405	.185	.0023	.149
			1.3000	1.000	.0152	1.000

$MW_{solv} = 85.65$

Mixture specific gravity of Solvent

$$= \left(\frac{.1}{.7917} + \frac{.199}{.8061} + \frac{.566}{.8684} + \frac{.185}{.8678}\right)^{-1} = .8506$$

$$V_{solv} = \frac{MW}{Sp\ gr} = \frac{85.65}{.8506} = 100.7$$

$MW_{polymer} = 15,200$ and $Sp\ Gr_{polymer} = .4087$

$$V_{polymer} = \frac{MW}{SpGr} = \frac{15,200}{.4087} = 37,191$$

$$m_1 = \frac{37,191}{100.7} \Rightarrow \underline{m_1 = 370}$$

$\underline{n_{solv} = .0152 \text{ lb mol}}$ and $\underline{n_p = .0000238 \text{ lb mol}}$

$$\Phi_{p_1} = \frac{(370)(.0000238)}{.0152 + (370)(.0000238)} \Rightarrow \underline{\Phi_{p_1} = .3668}$$

b) Calculate Φ_{p_2} at end of step (2).

(This rigorously involves trial & error calculation of activity coefficient and final conditions of step (1). In other words the final answer must be approximately known before the entire calculation can be completed.)

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Solvent composition:

Component	lb	w.f.	mol	m.f.
Acetone	.0020	.004	.000034	.007
MEK	.0232	.051	.000322	.067
Toluene	.2780	.612	.003019	.629
Xylene	.1513	.333	.001426	.297
	.4545	1.000	.0048	1.000

$\overline{MW}_{solv} = 94.69$

Mixture specific gravity of solvent

$$= \left(\frac{.004}{.7917} + \frac{.051}{.8061} + \frac{.612}{.8684} + \frac{.333}{.8698} \right)^{-1} = .865$$

$V_{solv} = \frac{94.69}{.865} = 109.5$ and $V_{polymer} = 37,191$

$$n_2 = \frac{37,191}{109.5} \Rightarrow \underline{n_2 = 340}$$

$\underline{n_{solv} = .0048 \text{ lb mol}}$ and $\underline{n_p = .0000238 \text{ lb mol}}$

$$\Phi_{P_2} = \frac{(340)(.0000238)}{.0048 + (340)(.0000238)} \Rightarrow \underline{\Phi_{P_2} = .6277}$$

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c) $\Phi_{P_1} / \Phi_{P_2} = z_1/z_2 = \left(\frac{.3668}{.6277}\right) = \underline{.58}$

② Calculate γ_1 and γ_2 via

$$\gamma = \exp\left\{\ln\left[1-\left(1-\frac{1}{in}\right)\Phi_P\right] + \left(1-\frac{1}{in}\right)\Phi_P\right\}$$

a) $\gamma_1 = \exp\left\{\ln\left[1-\left(1-\frac{1}{370}\right)(.3668)\right] + \left(1-\frac{1}{370}\right)(.3668)\right\}$

$\underline{\gamma_1 = .914}$

b) $\gamma_2 = \exp\left\{\ln\left[1-\left(1-\frac{1}{340}\right)(.6277)\right] + \left(1-\frac{1}{340}\right)(.6277)\right\}$

$\underline{\gamma_2 = .700}$

c) $\underline{\gamma_2/\gamma_1 = .766}$

③ Using B.Y. Hill correlations for γ_{avg} (last page of memo)

$\gamma_{avg}/\gamma_1 = .894$

$\therefore \gamma_{avg} = \gamma_1(\gamma_{avg}/\gamma_1) = (.914)(.894)$

$\boxed{\gamma_{avg} = .817}$

R.J. Petrochko

3-7-78

APPENDIX III

CALCULATION OF γ_{SOLV}, STEP (2)

Activity Coefficient of Solvent in Varnish - Step (2)

Rather than go through double-step procedure used to calculate $\gamma_{step(1)}$, conservatively estimate

$$\gamma_{avg\ step(2)} = \gamma_{@\ end\ of\ step(2)}$$

(see Appendix II. for physical properties)

$n_{solv} = .000371$ lb mol assuming primarily Xylene left @ MW ≅ 105.

$n_p = .0000238$ lb mol

$$V_{solv} = \frac{105}{.8698} = 120.7$$

$$m = \frac{37.191}{120.7} \Rightarrow \underline{m = 308}$$

$$\Phi_p = \frac{(308)(.0000238)}{.000371 + (308)(.0000238)} \Rightarrow \underline{\Phi_p = .9518}$$

$$\gamma = \exp\left\{\ln\left[1-\left(1-\tfrac{1}{308}\right)(.9518)\right] + \left(1-\tfrac{1}{308}\right)(.9518)\right\}$$

$$\boxed{\gamma = .132}$$

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3-7-78