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To: SPI Technical Subcommittee of the VCM Steering Committee

Subject: Report on Task Assignments 4.1 and 4.2
(B.F.Goodrich Chemical Company)

Task 4.1

Analysis of the postulate by Seymour Gilbert (Rutgers) of a non-linear partitioning of monomer from polymer to food simulating solvents when initial concentrations of monomer are low.

4.11 Is the postulate sound scientifically?

Yes. The "Gilbert postulate" is experimentally true and therefore scientifically sound, though not original with Gilbert.

The non-linear partitioning of VCM between PVC and vapor has clearly been shown in work published by B.F.Goodrich (A. R. Berens. Polymer Preprints, 1974). Gilbert's data extend this finding to PVC/water, PVC/oil, and PVC/hexane partitioning of VCM. Similar observations have been known for many years in other glassy-polymer/vapor systems. These observations have led to a "dual-mode sorption" hypothesis (true dissolution plus adsorption in "holes"), but the exact mechanism of such sorption behavior is still a subject of scientific controversy. Very recently (AIChE meeting, Boston, Sept. 1957) D. R. Paul of the University of Texas, has shown that immobilization of the adsorbed species is not necessary to account for such behavior.

4.12 Can we develop data to prove the postulate? How? When?

The main question about the "Gilbert postulate" is not whether it's real (we've already shown that it is), but whether it is large enough to be of any consequence in establishing the safety (lower VCM migration) of PVC products. Based on Gilbert's data it does not appear that the effect will be large. Nor does our present understanding lead to any theoretical prediction of large changes in diffusivity or the partition coefficient as VCM concentration approaches zero.

Task 4.2

Analysis of the possibility of marked different rates of partitioning of monomer from polymer to food simulating solvents as a function of initial concentration. Also partitioning into air.

4.21 Is this possibility sound scientifically?

Yes. Again, published BFG work (A. R. Berens, ibid.) has indicated a decreasing diffusity of VCM in PVC with decreasing VCM concentration. Gilbert has so far added no further experimental evidence. Such concentration-dependence of diffusivity is well-known in many other cases of rigid polymers with solvent vapors. Thus, this is another postulate that is true, hence sound, but not new.

4.22 Can we prove this mathematically? Experimentally? How?

The questions raised by these "Gilbert postulates" thus are not those of validity or soundness, but simply of magnitude: Are the changes in partition and diffusivity of VCM at very low concentrations in PVC sufficiently large that the migration of VCM into the contents of PVC pipes and bottles is significantly lower or slower than predicted by models which assume constant diffusivity and partition (such as Ethyl Corp. or B.F.Goodrich models)? The final answer can come only from careful experiments at low VCM levels. Such experiments are now being planned at B.F.Goodrich. It is our present opinion, however, that the "Gilbert effect" will not be large enough to substantially alter the predicted rates or extents of VCM migration.

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Gilbert's Data on VCM/PVC Partition Coefficient

[Unplasticized PVC]

Solvent	C_1 (g/g) in Solution	C_2 (g/g) in Polymer	$K = C_2/C_1$
Oil	5.55×10^{-2}	3.48×10^{-2}	0.627
	1.14×10^{-2}	9.67×10^{-3}	0.848
	5.02×10^{-3}	7.02×10^{-3}	1.39
	6.95×10^{-4}	1.37×10^{-3}	1.97
	4.54×10^{-4}	6.69×10^{-4}	1.47
	2.30×10^{-5}	8.42×10^{-5}	3.66
	4.00×10^{-6}	1.62×10^{-5}	4.05
Hexane	1.53×10^{-1}	3.76×10^{-2}	0.246
	2.20×10^{-2}	1.37×10^{-2}	0.623
	9.33×10^{-3}	5.94×10^{-3}	0.637
	1.33×10^{-3}	1.39×10^{-3}	1.05
	4.17×10^{-4}	9.19×10^{-4}	2.20
	3.33×10^{-5}	6.62×10^{-5}	1.99
	2.73×10^{-6}	5.89×10^{-6}	2.16
Water	2.43×10^{-5}	1.50×10^{-3}	61.7
	7.10×10^{-6}	6.75×10^{-4}	95.1
	7.20×10^{-6}	6.75×10^{-4}	93.8
	3.28×10^{-6}	3.56×10^{-4}	10.9

[Plasticized PVC]

Solvent	C_1 (g/g) in Solution	C_2 (g/g) in Polymer	$K = C_2/C_1$
Oil	5.21×10^{-2}	3.18×10^{-2}	0.610
	1.23×10^{-2}	6.42×10^{-3}	0.522
	6.35×10^{-3}	4.00×10^{-3}	0.630
	1.06×10^{-3}	6.68×10^{-4}	0.630
	5.51×10^{-4}	2.65×10^{-4}	0.481
	5.42×10^{-5}	3.01×10^{-5}	0.555
	9.75×10^{-6}	6.29×10^{-6}	0.645
Hexane	1.35×10^{-1}	4.32×10^{-2}	0.320
	2.68×10^{-2}	7.56×10^{-3}	0.282
	1.20×10^{-2}	3.26×10^{-3}	0.272
	2.36×10^{-3}	3.73×10^{-4}	0.158
	1.04×10^{-7}	3.16×10^{-4}	0.303
	8.59×10^{-5}	1.66×10^{-5}	0.193
	6.48×10^{-6}	2.22×10^{-6}	0.343
Water	9.20×10^{-5}	1.31×10^{-3}	14.2
	3.48×10^{-5}	5.74×10^{-4}	16.5
	1.90×10^{-5}	2.94×10^{-4}	15.5
	8.50×10^{-6}	1.43×10^{-4}	16.8
	8.45×10^{-6}	1.43×10^{-4}	16.9
	2.54×10^{-6}	2.73×10^{-5}	10.7