When the Group met in Bristol in June 1974, it was decided that David Williams should be asked whether he was willing to continue in his capacity as Newsletter Editor - a function which he had fulfilled most ably since the inception of the Group. However it transpired in September that he had moved to a new position with the Foster Grant Co. and was consequently obliged to resign from the Group since he would no longer be active in Polymer Colloid research.

Several members have suggested that I should now act as Newsletter Editor. Unfortunately this suggestion came at a time when the British government was refusing to supplement the universities' grant at all to compensate for the extremely high rate of inflation in Britain which is at least double that prevailing in the U.S. and much beyond anything which had been budgeted for. Consequently drastic economies were being instituted so that the time did not seem propitious to request additional expenditure. This has led to a hiatus in the circulation of the Newsletter which this economy issue will partially overcome.

It now seems that it should be possible to issue Vol. 5 No. 1 in October provided all members send their contributions to reach me by Monday 15th September. Contributions which arrive late will have to be held over till the January issue.

Increase in membership of the Group increases both the bulk of the Newsletter and the number of copies required. The reprographic cost (with no labour charge) had reached about £ 1 per copy and postage would be about £ 1 also when transatlantic copies are sent by Air Mail. And there are currently 17 members. Some members therefore feel that the time has come when an annual subscription will have to be raised but this would be unwelcome at a time when the Scientific Societies' subscriptions are being increased at a rate greatly in excess of members' ability to pay them! Alternatively it may be possible to raise a Fund to cover the cost of production and distribution of the Newsletter: this might, however, prove difficult in a period of recession in which many prominent industrial firms seem to be in financial difficulties. Additionally Funds, Accounts, etc. generate much work in their administration! We should be able to resolve these problems whilst at Trondheim.

In the meantime, members are asked to confine their Newsletter copy to two (or, at most, three) filled pages typed single-spaced.

A-J- Dunn.

New Members

Dr D.C.Blackley, National College of Rubber Technology, The Polytechnic of North London, Holloway, LONDON N7 8DB, England.

Dr D.W.J.Osmond, I.C.I. Ltd., Paints Division, Wexham Road, SLOUGH, Buckinghamshire England.

Change of Address

Dr J.L.Gardon, Coatings & Ink Division, M & T Chemicals Inc., 26701 Telegraph Road, Southfield, Michigan 48076, U.S.A.

Dr D.J.Williams, Foster Grant Co. Inc., 289 North Main St., Leominster, Massachusetts 01453, U.S.A. (Requests to be kept on member's mailing lists)

Prof M. Nomura, Dept of Industrial Chemistry, Fukui National University, Fukui, Japan

Difficulty had been experienced in finding a custom synthesis firm willing to attempt the preparation of azo-bis(methyl isobutyronitrile sodium sulphonate) but a quotation of £ 265 for 100 g. Although this was close to the price of gold powder, it appeared that it was in the normal range for such projects. However it might be that a lower estimate would be obtainable if any group member were able to report a good yield in a smaller scale preparation.

Dr J.L.Gardon (M & T, Chicago) discussed difficulties experienced in formulating latexes to give high gloss industrial coatings. These were needed to meet Federal legislation against air pollution caused by solvent evaporation in the processes used hitherto. Industrial finishes had to be suitable for oven drying: air drying was too slow.

High gloss (90-100) could be achieved: pigment wetting, particle size, and molecular weight were vital factors. Surfactant-free latexes of partially neutralised carboxylated copolymers were used

Formulation was much more complicated than for a trade sales paint, up to 12 ingredients might be needed.

1. Application had to be by spray-gun: for this it was vital that the coating be thixotropic but a theoretical understanding of this phenomenon in latexes was lacking.

2. A thermosetting resin was required for metal coating. Cross-linking of hydroxyl groups by melamine was used.

3. A pigment which might need a surfactant to disperse it.

4. An organic solvent forming an azeotrope with water was used to speed drying. This also acted as a coalescent - a temporary plasticiser to aid film formation. Films formed without this at room temperature were not hard enough for industrial coatings.

5. A filler: this affected both drying rate and thixotropy.

6. An anti-foam.

7. An amine (e.g. melamine) both to cross-link the resin and maintain a high pH after application to prevent rusting of the steel substrate.

8. A thickener e.g. hydroxyethyl cellulose was needed for air-gun application (the airless gun was not suitable for latexes).

9. Waxes to promote abrasion resistance.

Dr Warson suggested that the solvent could be omitted if an amine which would dissolve the latex were used: hexamethoxymelamine might be suitable. Dr Gardon said that odours of amine and formaldehyde were a problem and a practical non-amine cross-linker was much needed.

On the Current Position in the Controversy over Williams's Core-Shell Morphology Dr Gardon said that it had to be accepted that seeded polymerisations do lead to a core-shell morphology even when the overcoating polymer is completely compatible with the seed. Apart from Williams's electron micrograph and tritiation experiments, Gardon had had evidence on the Minimum Film-forming Temperature of styrene-butadiene latexes in the 40:60 - 60:40 composition range in which the composition of the overcoating differed from that of the seed.

What was controversial was the kinetic, molecular-weight, and thermodynamic evidence for the occurence of core-shell morphology in single-charge experiments. The molecular-weight evidence had been conclusively disproved by the work of Kamath presented by Morton at the A.C.S. Meeting earlier in the week. It was not true that Grancio and Williams's results indicated a constant rate in interval II: a (conversion)/ t versus conversion plot to eliminate the effect of the induction period, the best fit to their points obtained by using statistical fitting procedures by a curve indicating rate increasing with conversion. Moreover the results of doubling the initiator concentration in the course of a run indicated the expected low increase in rate which was significant at the 80% level. The experimental points showed bad scatter necessitating the use of statistical techniques. DiMarzio's statistical thermodynamic treatment could not prove assumptions implicit in the model by stating them in a formal mathematical way. The assumption that fixing of a polymer chain-end at the particle surface by a hydrophilic

Particle Size Analysis by Higher Order Tyndall Spectra

Three cases of unexpected behavior have been observed in the measurement
of particle size of PVC latex by Higher Order Tyndall Spectra. These are (1) the
diameter calculated from the observation angle of the first red order was
generally the largest of the red diameters, especially for particles larger
than 7500Å, (2) the diameters calculated from the green bands were always larger
than those calculated for red bands and (3) the diameters calculated from the
green bands get progressively larger with increasing order. The data are
tabulated in Table 1. These anomalies do not appear to be peculiar to PVC
latexes alone but appear in the data of Maron (J. Colloid Sci., 18 193, 1963;
ibid. 19 658, 1964) as shown in Table 2 and also in data on Polystyrene
obtained by Dr. Berens, B.F.Goodrich Research Center as shown in Table 3.

We believe the larger values obtained from the angular dependence of
the first red order manifest the fact that these systems are not truly mono-
disperse. The scattering from the excessively large particles will be greatest
at the low angles thus causing the order to be shifted to low angles in this
region. Because of the nature of the sine function, a small angular shift will
produce a considerable effect on the diameter.

The other two discrepancies lead us to question the basic assumption which
is made by Maron, that the maxima in the R/G ratio occur when the intensity of
the green light is at a minimum, and the maxima in the G/R ratio occur when the
intensity of the red light is at a minimum. The data that is included in
Tables 1, 2, & 3 all seem to indicate that the first part of the assumption
is valid, but not the latter.

We are aware of the importance of using the correct wavelengths,
$\lambda_g = 3506Å$, $\lambda_r = 4740Å$. This data could be interpreted to say that the maxima
in the R/G ratio to occur when the intensity of the green light is at a
minimum and the the maxima in the G/R ratio occur when the intensity of the
red light is at a minimum but only for small angles.

We propose that for calculating diameters from green orders a better
assumption would be to consider that the maxima in the G/R ratio occur when
the intensity of the green light is at a maximum. Thus, instead of using
equation (1) as the working equation to calculate green diameters, equation
(2) would be used.

$$D = (k_i \lambda'_r)/\sin (g_i/2) \qquad\qquad (1)$$

$$D = (K_i \lambda'_g)/\sin (g_i/2) \qquad\qquad (2)$$

Green diameters calculated by this second equation are included in Tables 1,
2, and 3. In each case better agreement with the red diameter is obtained.

Another reason for suspecting equation (1) is that the constants
$C_G = k_i\lambda'_r$ are not consistent with the constants $C_R = k_i\lambda'_g$, that is, a

progressively increasing value of the constants is not maintained with the increasing order of the spectra. However, when $K_i \lambda'_g$ is considered in place of $k_i \lambda'_r$ the constants do get progressively larger and in an orderly manner (Table 4). This is true for m = 1.16 and m = 1.17. Note that changing λ'_r from 5350 to 4695 does not correct this fluctuation.

Lastly, we find that the sin $(g_i/2)/\sin (r_i/2)$ is not a constant independent of m and i but rather a variable dependent on i and affected by α. A summary of our results are included in Table 5.

The sin ratio for the small particles is in very good agreement with the K_i/k_i ratio. The higher values of the sin ratio for particles have $r_i < 28°$ again reflects the difficulty in accurately determining the first red band. This agreement with the K_i/k_i ratio again indicates that the green angles should be considered as maxima.

Applying the numbering test to samples of various m values demonstrated repeatedly that the sin $(g_i/2)/\sin (r_i/2)$ ratio is consistent with K_i/k_i values and that the sin $(g_i+_i/2)/\sin (g_i/2)$ is in agreement with K_i+_i/K_i and not with k_i+_i/k_i. Three examples (m = 1.17, 1.20, and 1.16) are included in Table 6.

Presently it is suggested that only the red diameters be used for particle size analysis as we are not pleased with the green diameter calculations. Finding the right wavelength for red light does not seem to be the true corrective measure because regardless of the value chosen, the constants $k_i \lambda'_g$ and $k_i \lambda'_r$ will eventually become disordered as was mentioned above. A second approach would be to assume that the effective red wavelength changes with angle and must be determined for each system. This would be very emperical, dependent both on the system and the observer, and seems unjustifiable if at the same time the green wavelength is considered constant for any angle of observation.

To summarize we have these basic questions:

1. What is the effect of polydispersity on the angular measurements as a function of order; that is, is the effect of polydispersity on the angular position of the first order greater than say for the fifth order?

2. For m = 1 , $R/G = \dfrac{I\theta(r)}{I\theta(g)}$ is a maximum when $I\theta(g)$ is zero and a minimum when $I\theta(r)$ is zero. Since for m > 1 $I\theta(r)$ and $I\theta(g)$ never equal zero is it not possible that the minima of the R/G function exist when $I\theta(g)$ is at a maximum rather than $I\theta(r)$ being at a minimum?

3. As indicated by the second and third minima of the R/G curve of Figure 1, is it not possible that maxima and minima in the R/G function can occur without minima and maxima occurring in either of the two individual intensity functions?

We would welcome your criticisms of this treatment of green HOTS data.

Edward A. Collins

Dr. Edward A. Collins

Table 1

Diameters of Polyvinyl Chloride (n=1.16) Calculated from ECTS Data

Color of Order	Order No.	CALCULATED DIAMETERS									
		214-7	190-14	190-3	190-30	190-10	45-99	45-104	199-04	199-05	199-9
Rod*	1	2965	4960	5190	5265	5815	6640	9150	10300	12460	14220
	2		5050	5290	5515	5695	6200	8300	10100	11410	14050
	3						7140	8690	10120	10970	13190
	4							8840	10190	11120	13210
	5									11340	12940
	6										12740
	AVE	2965	5005	5240	5390	5755	6607	8738	10280	11580	13511
Green ±	1	----	5180	5540	5490	5860	7180	9040	10500	11120	12810
	2		6175	6175	6320	6590	7960	9340	11470	12520	14940
	3						9050	10100	11720	12920	15510
	4								12325	13090	15630
	5									14750	16210
	6										16750
	AVE	----	5678	5858	5905	6225	8063	9520	11504	12996	15305
Green +	1	----	4980	5230	5180	5530	6760	8520	9955	10720	12100
	2		5330	5330	5490	5690	6950	8150	9910	11000	12300
	3						7430	8470	9710	10320	12200
	4								9960	11120	12760
	5									11700	12920
	6										13100
	AVE	----	5155	5280	5333	5610	7047	8380	9882	11072	12700
Diameter Min-Max	$\lambda=4360$	----	----	5182	4950	----	----	----	10104	11426	----
	$\lambda=5460$	----	----	5070	5033	----	----	----	10009	11211	----

* $D = (k_1\ 3930)/\sin(r_1/2)$
± $D = (k_1\ 5350)/\sin(g_1/2)$
+ $D = (K_1\ 3930)/\sin(g_1/2)$

Table 2

Diameters of Butadiene-Styrene Latices Calculated from Red and Green Orders
(m=1.17)

Color of Orders	Order No.	Calculated Diameters - A			
		2713	197	697	597
Red	1	5060	6840	8610	11000
"	2	5170	6510	7930	9360
"	3	----	6410	7700	9050 ⎫ 9240
"	4	----	----	8060	9150 ⎬
"	5	----	----	----	9500 ⎭
AVE of Red Diameters		5115	6587	8075	9612
Green	1	5250	6890	8330	10100
"	2	----	7000	8640	10400
"	3	----	----	8980	10600
"	4	----	----	----	11200
AVE of Green Diameters		5250	6945	8650	10575
Average		5160	6730	8340	10040
% Dev.		± 1.3	± 3.2	± 4.4	± 6.9
D Min. Int.		5170	6580	8430	10100
% Dev.		- 0.2	+ 2.3	- 1.3	- 0.6
Green $D = (E_t\ 3505)/\sin(\varepsilon_t/2)$		4970	6530	7890	9580
			6060	7500	9040
				7480	8840
					9230
AVE of Green Diameters		4970	6295	7623	9173

Table 3

Diameters of Dow Polystyrene LS-057-A Calculated from EM Data ($\eta = 1.20$)
(E. M. = 11710 Å)

Order	Angle LaMer and Plesner	Berens	Sin /2 (Berens') Date	$D=k_1\dfrac{3930}{Sin(r_1/2)}$	$D=k_1\dfrac{4830}{Sin(g_1/2)}$	$D=k_1\dfrac{3930}{Sin\, g_1/2}$
R_1	24	21	0.1821	13950		
G_1	--	35	0.3005		10360	10840
R_2	45	45	0.3826	11420		
G_2	--	56	0.4694		11370	10950
R_3	65	66	0.5445	11320		
G_3	--	79	0.6360		11060	10950
R_4	89	91	0.7125	11170		
G_4	--	105	0.793		12290	11060
R_5	119	123	0.878	11000		
G_5	--	137	0.923		12800	11420

Relation of Intensity Minima to Positions of Red and Green HOTS Orders at $m = 1.20$ (Calculated from Mie Theory for $D = 6025 \text{Å}$, $\lambda_g' = 3506 \text{Å}$, $\lambda_r' = 4740 \text{Å}$)

$\alpha = 40$ $\lambda_r' = 4740 \text{Å}$

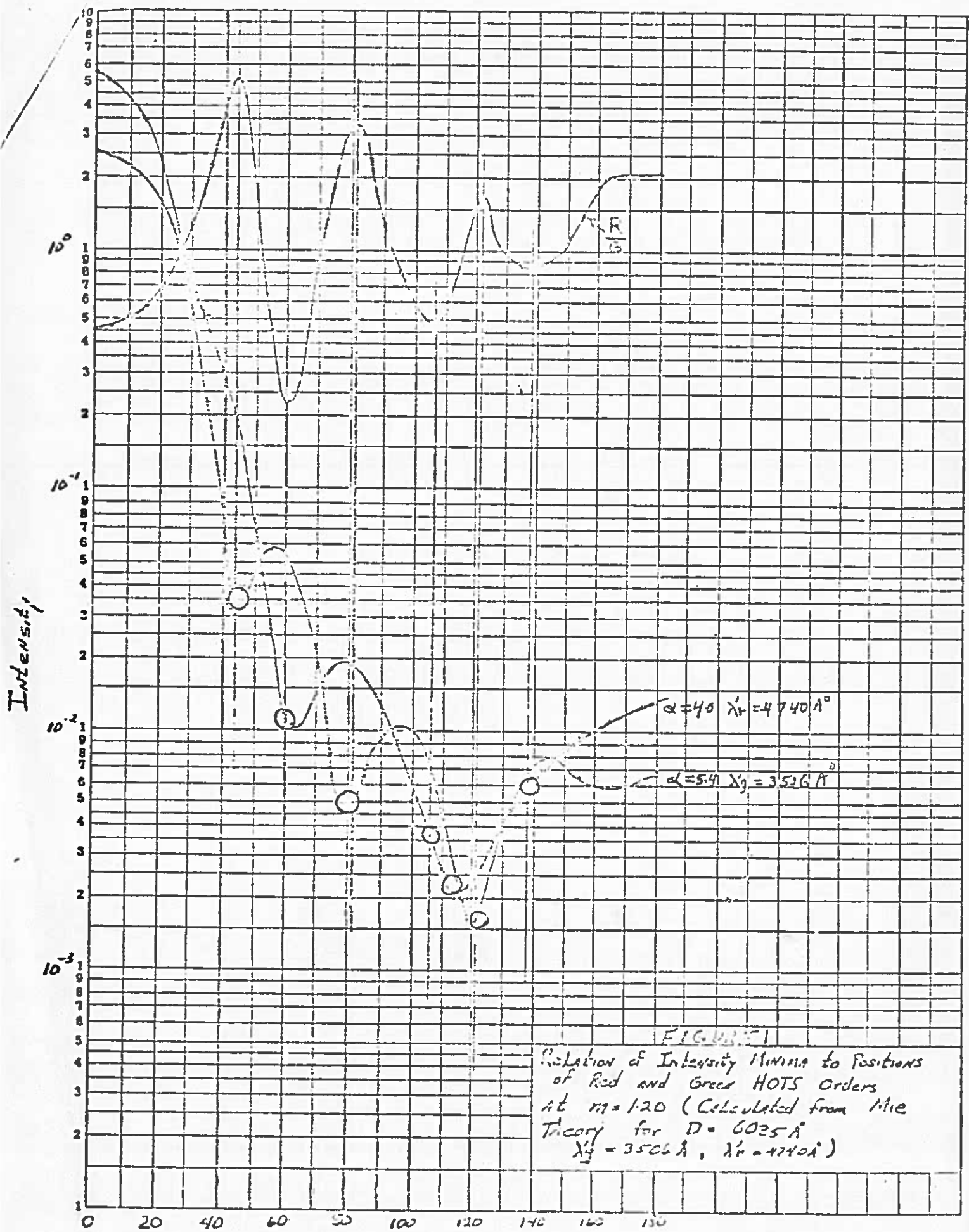$\alpha = 5.4$ $\lambda_g = 3516 \text{Å}$

FIGURE 1

Table 4

Working Constants (k_1 ') for Butadiene-styrene Latices
(m=1.17, k_1=0.656) and Polyvinyl Chloride (m=1.16, k_1=0.660)

Order	Butadiene-Styrene		Polyvinyl Chloride		
	$C_{R1}=k_1$ 3506 $C_{G1}=k_1$ 4740	$C_{R1}=k_1$ 3506 $C_{G1}=k_1$ 3506	$C_R=k_1$ 3930 $C_G=k_1$ 5350	$C_R=k_1$ 3930 $C_G=k_1$ 3930	$C_R=k_1$ 3930 $C_G=k_1$ 4695
R_1	2300	2300	2593	2593	2593
G_1	3120	2955	3530	3320	3098
R_2	3960	3960	4460	4460	4460
G_2	5370	4660	6075	5250	5730
R_3	5580	5580	6290	6290	6290
G_3	6960	6310	8960	7100	7520
R_4	7210	7210	8135	8135	8135
G_4	9750	7940	11070	8950	9720
R_5	8810	8810	9920	9920	9920
G_5	11950	9550	13510	10760	11870
R_6	10420	10420	11725	11725	11725
G_6	14130	11150	15960	12550	14040
R_7	12040	12040	13550	13550	13550
G_7	16310	12730		14350	16200

Table 5

$\sin(c_i/2)/\sin(z_i/2)$ as a Function of i and α

	$\dfrac{\sin(c_2/2)}{\sin(z_1/2)}$	$\dfrac{\sin(c_3/2)}{\sin(z_2/2)}$	$\dfrac{\sin(c_4/2)}{\sin(z_3/2)}$
Particles having $r_1 < 20°$	1.480	1.246	1.165
Particles having $r_1 > 20°$	1.297	1.173	-----
F_i/z_i	1.283	1.176	1.130

Table 6

Butodiene-Styrene sample No. 597 (n=1.17)

Rod	Diameter	Sin θ/2	Exp $\dfrac{Sin(r_{i+1}/2)}{Sin\ r_i/2}$	Theory k_i+_1/k_i	Exp $\dfrac{Sin(r_i/2)}{Sin(r_1/2)}$	Theory k_i/k_1
1	11000	0.209	2.023	1.720	1.479	1.203
2	9360	0.423	1.459	1.410	1.220	1.176
3	9090	0.617	1.270	1.292	1.052	1.130
4	9150	0.708	1.173	1.223	1.103	1.102
5	9500	0.988				

Green	Diameter	Sin θ/2	Exp $\dfrac{Sin(g_{i+1}/2)}{Sin(g_i/2)}$	Theory k_i+_1/k_i	Theory k_i+_1/k_i	
1	10100	0.509	1.670	1.720	1.570	
2	10400	0.516	1.272	1.410	1.354	
3	10600	0.656	1.531	1.292	1.259	
4	11200	0.873				

Dow Polystyrene LS-057 - A (n = 1.20)

Rod	Sin θ/2	Exp $\dfrac{Sin(r_{i+1}/2)}{Sin(r_i/2)}$	Theory k_i+_1/k_i	Exp $\dfrac{Sin(g_i/2)}{Sin(r_1/2)}$	Theory k_i/k_1
1	0.1821	2.100	1.720	1.650	1.203
2	0.3826	1.422	1.410	1.227	1.176
3	0.5445	1.310	1.292	1.168	1.130
4	0.7125	1.232	1.223	1.113	1.102
5	0.878			1.082	1.083

Green	Sin θ/2	Exp $\dfrac{Sin(g_{i+1}/2)}{Sin(g_i/2)}$	Theory k_i+_1/k_i	Theory k_i+_1/k_i
1	0.3005	1.562	1.720	1.570
2	0.4694	1.355	1.410	1.354
3	0.6360	1.247	1.292	1.239
4	0.793	1.163	1.223	1.202
5	0.923			

ITC 199-85(-n),16)

Rod	Sin θ/2	Exp $\frac{Sin(r_1=1/2)}{Sin(r_1/2)}$	Theory k_1+1/k_1	Exp $\frac{Sin(g_1/2)}{Sin(r_1/2)}$	Theory E_1/E_1
1	0.1992	1.920	1.720	1.545	1.203
2	0.3825	1.462	1.410	1.247	1.176
3	0.559	1.277	1.292	1.174	1.130
4	0.714	1.212	1.223	1.125	1.102
5	0.866	1.116	1.182	1.064	1.083
6	0.966				

Green	Sin θ/2	Exp $\frac{Sin(g_1=1/2)}{Sin(g_1/2)}$	Theory k_1+1/k_1	Theory E_1+1/E_1
1	0.3092	1.542	1.720	1.570
2	0.477	1.376	1.410	1.384
3	0.656	1.226	1.292	1.259
4	0.804	1.146	1.212	1.202
5	0.921			