Specifying Slurry Surfacing Emulsion Quality: Particle Size and Size Distribution Mikael Engman[a], Alan James[b], David Needham[c] & Tony Ng[d]

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Abstract
Current specifications for slurry surfacing emulsions do not allow 'good' and 'bad' emulsions to be distinguished without performance tests.

One of the important properties of slurry emulsions is their particle size and size distribution. Smaller average particle size is associated with rapid cohesion development. In order that changes in this important parameter can be related to performance in the field and so lead to quality improvement, a reproducible method of determining particle sizes is required.

In an effort to develop a standardized procedure for measuring and describing the particle size and size distribution of slurry emulsions, the four Akzo Nobel asphalt laboratories have cooperated in a round robin test of the Coulter LS230 particle sizer.

Introduction
The particle size distribution of an asphalt emulsion can influence physical properties such as viscosity and settlement [1-3]. Typically emulsions with smaller average particle size and a narrow particle size distribution have higher viscosities and lower settlement (Figure 1). However, of more interest is the influence of asphalt droplet size on the performance of the slurry itself.

**Figure 1: Effect of emulsion particle size on emulsion viscosity**
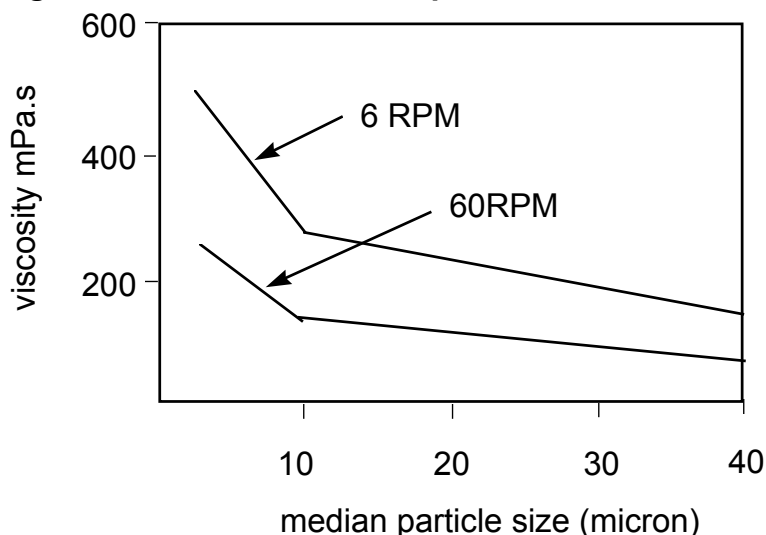
Viscosities are shown at two shear rates

The early performance of slurry surfacing depends on the interaction of the emulsion and the other components of the mix, particularly the aggregate. On the one hand the emulsion must provide a mix time sufficient to allow paving and on the other it must react quickly with the aggregate in the surfacing so that the road can be opened to traffic. It has been shown that particle size of the emulsion droplets affects the rate of cohesion build-up in slurry surfacings and other cold mixes [1] and some typical data is presented in Figure 2.

Figure 2: Effect of particle size on cohesion development.
A, B and C represent pairs of emulsions prepared from 3 different binder types (polymer-modified asphalts). The emulsions in each pair differ only in particle size. All emulsions contain 1.8% Redicote® E-849 as the primary emulsifier.

Labels on bar indicate median particle sizes in microns
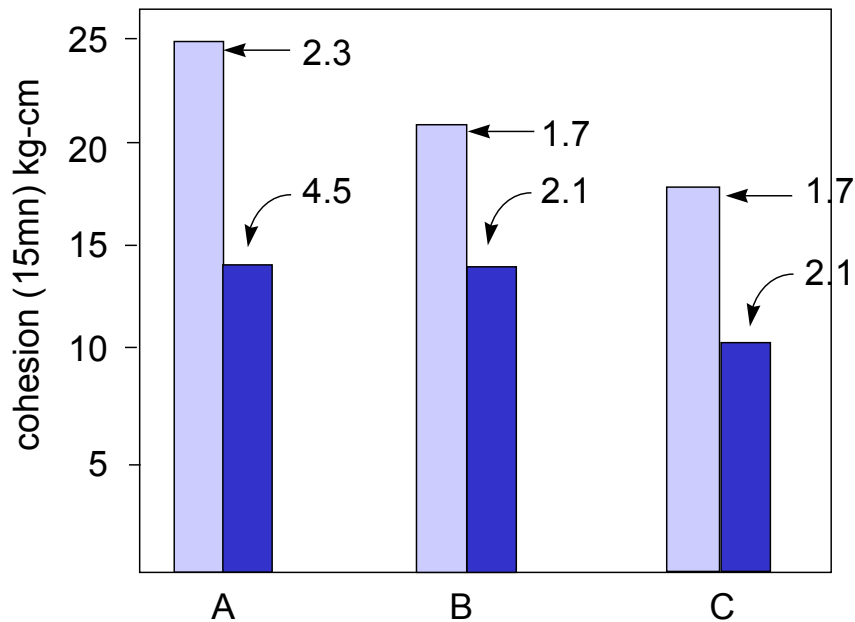
While various theories have been proposed to explain the setting behavior of emulsions in contact with aggregate, it has been found that the particle size distribution of the asphalt droplets can influence the process in several ways [1,4]. First, the particle size distribution determines the interfacial area between asphalt and water and this interfacial area is related to the level of 'free' surfactant in the emulsion. Free surfactant is that emulsifier which is not bound to the surface of the asphalt droplets but rather is in solution or micellar solution in the water phase. Free emulsifier can more quickly adsorb onto the surface of the aggregate than the droplets of asphalt themselves and adsorbed emulsifier modifies the surface charge of the aggregate and reduces its reactivity to the asphalt droplets. At a particular emulsifier content, the smaller the average particle size then the less free emulsifier is to be expected, and the faster the reaction.

Secondly, the size of the droplets directly affects their mobility towards the surface of the aggregate under the influence of the surface charge, since smaller particles move faster. A third effect relates to the ability of the emulsion drops to penetrate agglomerated fines in the mix - small droplets have a better penetrating power and react in a different way with fines [5].

Whatever the mechanism, the fact is that particle size has been shown to influence the setting rate of emulsions - for a particular emulsion recipe, an emulsion with the smaller particle size will normally set more quickly and cohesion build-up is faster. By determining the statistical relationship between particle size and field performance, there is scope for quality improvement in the slurry process either by setting limits on the variability of emulsion particle size or by setting limits on the size itself. However, for this process a good measurement of particle size is required. Since the emulsion supplier and emulsion user are not normally the same company, a method must be developed which gives reproducible results on different particle sizing machines.

National specifications for emulsions normally only specify the content of oversize particles greater than 150 or 800 microns, for example, determined by screening. These particles normally represent less than 0.2% by weight of the asphalt and tell us little about the average particle size of the emulsion. Thus it is not very useful to relate practical field performance to this specification item.

Several commercial machines are available for the particle sizing of emulsions based on light scattering, sedimentation, disc centrifuge, microscopy and the electrozone technique and most of these have been applied to asphalt emulsions [6-8]. However, the reproducibility and repeatability of the sizing methods have not been reported for bitumen emulsions. Akzo Nobel has the same model of sizer in each of its four asphalt test laboratories [7] and this has provided the opportunity to compare the results using slurry surfacing and other asphalt emulsions. Four laboratories is too small a number for an in-depth study of the reproducibility of a test method but could give a preliminary indication of the repeatability of the particle size data generated, to select parameters which show good reproducibility and to develop a test procedure for particle sizing which as far as possible minimizes differences in the results between laboratories.

Equipment
The Akzo Nobel laboratories have Coulter Model LS230 particle sizers which use a laser light scattering technique combined with a polarized light detection system to determine sizes in the range 0.02-2000 micron. From the intensity of the scattered light at different angles, a particle size distribution can be calculated [9-10].

In practice a few drops of emulsion are dispersed in water and pumped through the equipment where a laser beam is shone through and a series of detectors measure the intensity of scattered light at different angles. The equipment

compares this intensity with that from the background (no sample) and calculates a particle size distribution.

Sample preparation
The aim of the particle size measurement in our tests was to measure the ultimate particle size of the asphalt droplets, rather than the size of any flocculated or agglomerated particle clusters which may be present in a concentrated emulsion. This is because the interfacial area is related to the sizes of the primary particles and any clusters would be quickly dispersed in the diluted and high shear conditions of the slurry mixer; it is also easier to reproduce a fully deflocculated state than a state with partial flocculation. Thus the sample was prepared in such a way that any clusters are dispersed on dilution in the machine.

The dilution of the emulsion in the sizing machine (ca. 0.2 ml in 1.5 liter of water) leads to a destabilization and there is also a tendency for the emulsion to 'break' onto the internal surfaces of the equipment, leading to a gradual increase in the background count and the need for frequent cleaning. This is particularly a problem with quick-setting emulsions.

We set out to find a treatment that both disperses the droplets and protects them from any agglomeration or coalescence in the equipment, so that the mean particle size would not change significantly over the period needed to make the test (a few minutes). One constraint was that high levels of surfactant stabilizer may lead to foaming in the equipment which gives erroneous size measurements.

To overcome the problem of dispersion, the emulsion is predispersed and pre-diluted by adding a surfactant solution. To overcome the problem of agglomeration or coalescence in the equipment a stabilizing solution is added to the sample pot before adding the predispersed emulsion. We found that the following treatment is effective with most cationic emulsions.

1) *Pre-dispersion of sample*
The sample is dispersed with its own volume of 2% Redicote E-11 solution (CSS emulsifier). It was found that the predispersed emulsion was stable for several days or even weeks and although it needed some agitation to disperse settled asphalt, the particle size did not change during storage.

2) *Stabilization of sample in the Coulter equipment*.
10ml of 2% nonionic surfactant solution (50 mole ethoxylate of nonylphenol) and 10ml of concentrated hydrochloric acid were added to the water tank on the equipment before adding the predispersed sample. The resulting pH was around 1.5.

Figure 3: Effect of insufficient stabilization: 1st, 2nd and 3rd runs on same sample.
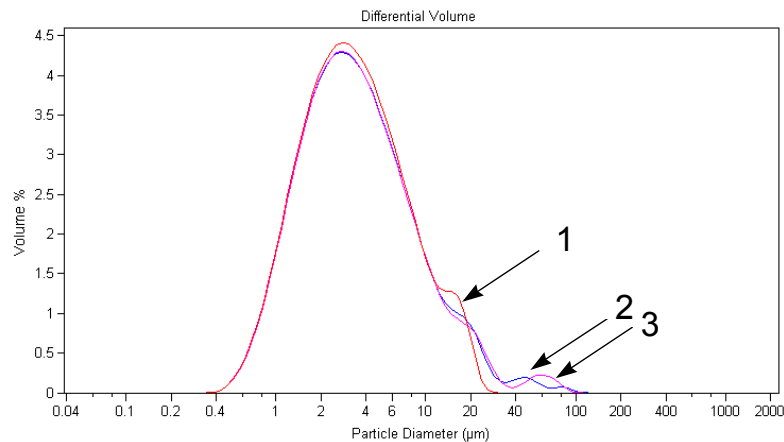
To ensure that the system was effectively stabilized, a repeat run is made within a few minutes of the first; if peaks or shoulders start to develop at the high end of the distribution and the median particle size increases significantly (more than 0.15 micron) then it indicates that the stabilizing system is not effective and the first reading is also suspect (see Figure 3). In this case the level or type of stabilizer was changed and the measurement repeated.

Occasionally, the repeat run actually shows peaks or shoulders on the high side of the distribution decreasing and a lower mean particle size, indicating that inadequately-dispersed agglomerates are breaking down. In this case the run is repeated until the agglomerates are completely dispersed and the size distribution does not change on the repeat run.

Run parameters
The operating instructions given by Coulter in the instrument manual were followed.

Although completely automated, the equipment allows the selection of run parameters such as run time, background run time, pump speed and rinse program to be chosen. In summary we found that the shortest run time (90 seconds) and a low pump speed of 20% gave the best control of foam and emulsion stability. The background was also run for 90 seconds.

Optical model
The derivation of the particle size distribution from the scattered light intensities requires a knowledge of the refractive indices of asphalt and water. The values assumed by the optical model provided by Coulter are water 1.332, asphalt 1.635 and asphalt imaginary refractive index 6.

The 'imaginary' refractive index is related to the absorbance of the particle.

Definition of particle size and size distribution

5

Asphalt emulsions contain a range of particle sizes and this range can be expressed in different ways. In common with most other workers we have expressed the size distribution in terms of the volume distribution (i.e. weight). Generally we have found that the relationship between particle volume and particle size is approximately log-normal (see Figures 3 and 4) in agreement with other workers and apparently consistent with a theory of emulsification in which droplets once formed in the colloid mill do not coalesce [11].

The size distribution curves can be compared directly but it is more convenient to extract a number or numbers representing the average particle size in order to compare the emulsions and relate their size to slurry performance. One of the targets of the work was to identify parameters which would be reproduced by the four laboratories. The standard deviation (S.D.) is generated by the Coulter software as a measure of the 'broadness' of the size distribution and these values are also given in the tables. The median diameter (D50) is a 'neutral' measure of the average particle size. Half of the sample expressed as weight exceeds the median. The arithmetic and geometric means, the mode and the median are shown for a typical distribution in Figure 3.

Other data such as the skewness of the curve and the kurtosis (deviation from true log-normal shape) are generated by the Coulter software but were not used in our analysis.

Repeatability of the measurement - One laboratory/operator
A preliminary study with one operator was carried out to form a baseline for acceptance or rejection of duplicate measurements for the reproducibility trials. A cationic quick set slurry emulsion was selected for this test. The results of 10 separate runs on the same sample (i.e. with rinsing of the equipment between each run and introducing a fresh sub-sample of the emulsion into the machine) are shown in Table 1. The S.D. values shown in Table 1 are a measure of the "width" of the size distribution.

Table 1: Size data from duplicate runs on CQS emulsion:

Run	a-mean(SD) (micron)	g-mean(SD) (micron)	median (micron)	mode (micron)	Surface area (cm^2/g)
10	4.695(4.36)	3.342(2.26)	3.186	2.787	24348
12	4.428(3.75)	3.259(2.19)	3.149	2.787	24550
14	4.927(4.94)	3.420(2.30)	3.228	2.787	24036
16	4.734(4.42)	3.365(2.26)	3.206	2.787	24197
18	4.613(4.14)	3.322(2.23)	3.182	2.787	24368
20	4.493(3.88)	3.283(2.20)	3.164	2.787	24481
22	4.644(4.18)	3.342(2.23)	3.200	2.787	24239
24	4.700(4.36)	3.348(2.25)	3.191	2.787	24295
26	4.758(4.51)	3.367(2.26)	3.204	2.787	24214
28	4.526(3.92)	3,299(2.21)	3.176	2.787	24415
Averages	4.65+/-0.15	3.33+/-0.05	3.19+/-0.02		24300+/-150

The average mean particle sizes calculated from the ten runs and the standard deviations of these averages are also shown in the table.

Each run was also repeated about 4 minutes after the first without rinsing to check that the stabilizing system was working satisfactorily, but these values were not used in the calculation of average emulsion particle size. The estimated variance between these repeats, expressed as standard deviation, was only ca. 0.1 micron for the arithmetic mean particle size, which suggests that the stabilizing system was working well and also that much of the error in the mean particle size came from the sampling of the emulsion and/or the background count.

The first graph in Figure 4 shows the distributions from the 10 tests. The variation between the runs on this emulsion occurred almost entirely in the 10-20 micron region where there was a shoulder on the distribution curve. The mode (peak position) was the same for all samples.

Reproducibility - Four laboratories/operators
A total of eight emulsions having a wide range of formulas (see Table 2), made on different colloid mills and consequently with a wide range of particle sizes, were tested according to the same procedure in the four laboratories. The Coulter sizers were not calibrated with any external standards and they were in the middle of their scheduled maintenance contracts - in short they were in a condition typical of their normal operation. The results from the four laboratories are shown in Table 3. Each laboratory did each determination twice with each sample and the average of these two determinations is given in the table.

Table 2: Description of test emulsions for round robin

Sample	Source	Emulsion type	Emulsifier	Comments
1	Willowbrook	CSS-1P	Redicote E-11	contains latex
2	Willowbrook	CQS	Redicote E-120	
3	Waco	CRS	Redicote EM44	contains solvent
4	Waco	CQS	Redicote 404	
5	Littleborough	micro	Redicote E-85	phosphoric acid
6	Littleborough	CRS	Redicote EM44	
7	Nacka	CSS-1h	Redicote 404	Russian asphalt
8	Nacka	CRS	Redicote EM44	contains solvent

Emulsion 6 showed evidence of breaking in the samples in two laboratories and was not included in the analysis.

The actual distributions obtained by the four laboratories for each of the emulsions tested are shown in Figure 4. Just as with the sample in one laboratory, the general features of the size distribution curves are well reproduced but differences can be seen especially in the region around 40 micron and to a lesser degree in the region below 1 micron. Average sizes like geometric mean and median which emphasize the 'body' of the curve are less affected by the differences than the arithmetic mean.

Table 3 : Results of particle sizing in the four laboratories.
Each value represents the average of two separate runs (i.e. with resample of the emulsion),
rounded to 2 or 3 significant figures.

Emulsion/Lab	a-mean(S.D.) (micron)	g-mean(S.D.) (micron)	median (micron)	surface area (cm^2/g)
1/L	6.8(5.7)	4.5(3.0)	5.26	39000
1/W	6.9(5.6)	5.0(2.5)	5.36	21000
1/C	6.5(4.8)	4.8(2.4)	5.29	22000
1/S	6.8(5.2)	5.0(2.5)	5.41	22000
2/L	7.9(7.5)	5.3(2.8)	5.66	26000
2/W	8.6(8.7)	5.6(2.7)	5.77	22000
2/C	7.4(6.5)	5.0(2.7)	5.47	27000
2/S	7.9(7.2)	5.3(2.8)	5.66	26000
3/L	5.2(5.0)	3.6(2.5)	3.58	30000
3/W	4.8(4.4)	3.5(2.2)	3.46	24000
3/C	4.9(4.3)	3.5(2.3)	3.54	26000
3/S	5.2(4.8)	3.7(2.3)	3.62	22000
4/L	4.9(4.7)	3.2(2.9)	3.76	47000
4/W	5.2(5.8)	3.4(2.8)	3.80	40000
4/C	4.8(4.5)	3.2(2.8)	3.80	45000
4/S	4.6(3.9)	3.2(2.9)	3.73	50000
5/L	3.1(2.9)	2.4(1.9)	2.23	29000
5/W	2.8(2.2)	2.3(1.8)	2.15	30000
5/C	2.8(2.1)	2.3(1.8)	2.19	30000
5/S	2.9(2.6)	2.3(1.9)	2.19	30000
7/L	5.3(5.5)	3.6(2.3)	3.52	23000
7/W	5.4(5.9)	3.7(2.3)	3.52	23000
7/C	4.6(3.7)	3.4(2.2)	3.43	24000
7/S	5.1(4.7)	3.6(2.3)	3.57	23000
8/L	6.7(5.6)	4.6(2.8)	5.13	33000
8/W	6.7(5.6)	4.7(2.5)	5.17	25000
8/C	5.6(3.5)	4.2(2.5)	4.98	30000
8/S	6.6(5.3)	4.6(2.7)	5.18	30000

L = Littleborough, England; W = Waco, Texas; C = Chicago (Willowbrook); S = Stockholm (Nacka)

The size data for the labs were averaged and a combined variance both for the individual emulsions and overall were calculated (Table 4)

Table 4: Averaged size data on test emulsions.
Each value is the rounded average of the original data with an estimate of the standard deviation for each emulsion based on the original measurements (before averaging duplicates) in the four laboratories.

| Emulsion	a-mean (micron)	g-mean (micron)	median (micron)	surface area (cm^2/g)
1	6.8+/-0.2	4.8+/-0.2	5.33+/-0.07	26000+/-8000
2	8.0+/-0.5	5.3+/-0.2	5.62+/-0.12	26000+/-3000
3	5.1+/-0.2	3.6+/-0.1	3.55+/-0.06	26000+/-3000
4	4.9+/-0.3	3.2+/-0.1	3.77+/-0.06	46000+/-4000
5	2.9+/-0.1	2.35+/-0.05	2.19+/-0.04	30000+/-500
7	5.1+/-0.4	3.6+/-0.1	3.51+/-0.07	23000+/-500
8	6.4+/-0.5	4.5+/-0.2	5.12+/-0.09	29000+/-5000

The within-laboratory and between-laboratory variances were calculated from all the test data assuming that the errors were not proportional to the particle size.

Expressed as estimates of the standard deviation, the results are as follows:

Between-laboratories (reproducibility)		_Within-laboratory (repeatability)_	
arithmetic mean	+/- 0.35 micron	arithmetic mean	+/- 0.20 micron
geometric mean	+/- 0.16 micron	geometric mean	+/- 0.07 micron
median	+/- 0.076 micron	median	+/- 0.043 micron
surface area	+/- 4300 cm^2/g	surface area	+/- 2100 cm^2/g

The estimates of the within-laboratory repeatability calculated from the data from the round robin were slightly higher than that calculated from a single emulsion (Table 1). The experience with a wider range of emulsions was that the surface area was not a very repeatable figure when the emulsion contained significant material less than 1 micron.

Figure 4: Overlays of size distributions from the 10 repeats of the CQS emulsion and the 8 repeats of samples 1-8 used in the round robin test.
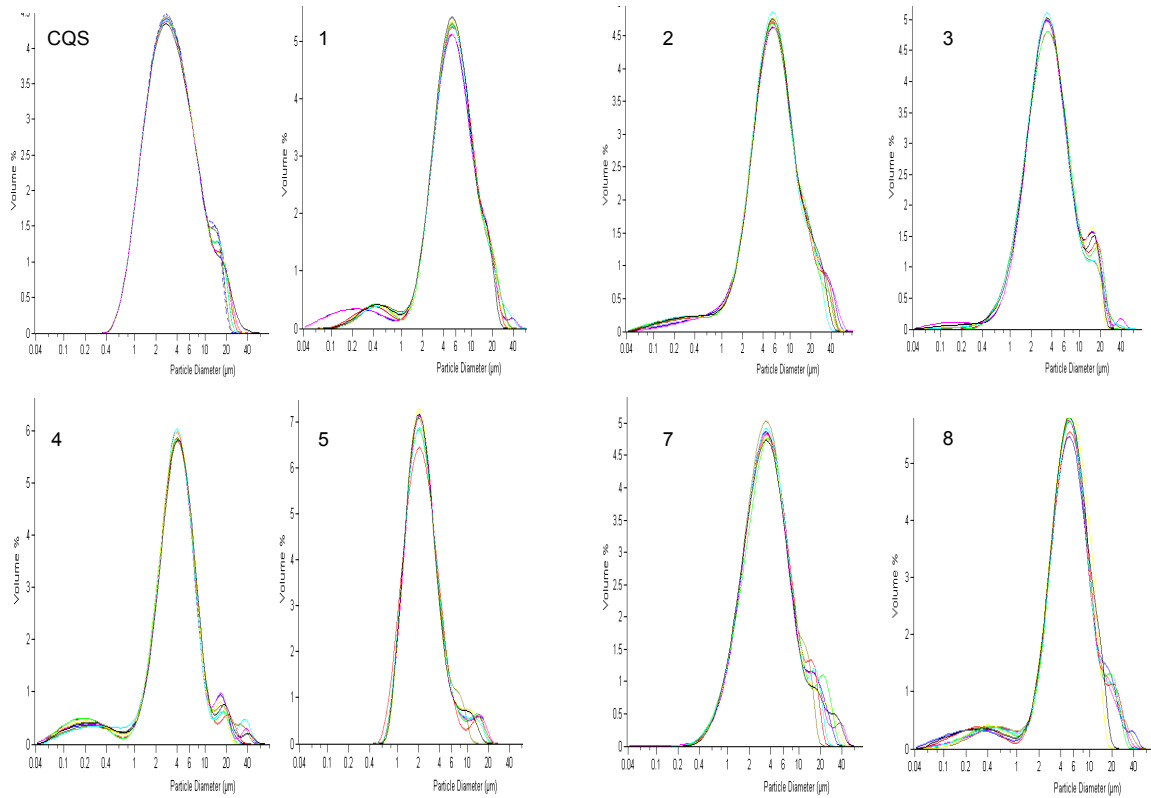
Assuming that these estimates of the standard deviations of the data are good and that laboratories routinely duplicate the size measurement and take an average of the results, then two results are not likely to differ between laboratories by more than about +/- 0.7 micron for the arithmetic mean, about +/- 0.3 micron for the geometric mean and about 0.15 micron for the median (95% confidence interval d2s).

Table 5 : Width of size distribution
Width of the size distribution expressed as standard deviation

Emulsion	Average S.D.	S.D./median %
1	5.3 +/- 0.4	100 +/- 8
2	7.5+/- 0.9	133+/-13
3	4.7+/- 0.4	132+/-10
4	4.7+/- 1.0	124+/-25
5	2.5+/- 0.4	111+/-16
7	5.0+/- 1.1	141+/-30
8	5.1+/- 1.1	99 +/- 19

The Coulter software calculates a standard deviation of the size distribution as a measure of the width of the distribution together with the arithmetic mean. The breadth of the distribution has been related to emulsion properties, especially emulsion viscosity. In our tests, the width was proportional to the median particle size (Table 5) and the ratio S.D./median did not differ significantly between emulsions indicating that the width measurement does not give additional information.

Discussion
The particle size distributions determined in the four laboratories were reasonably close but differed in detail, particularly in the region from 40-100 micron. The differences do not seem to be related to the size measurement *per se* but rather to the sample preparation. It is possible that some deterioration in the samples occurred in their transport between laboratories meaning that the differences seen are real. Or, it is possible that the pumps on some machines impose more stress on the emulsions and so more stabilization is required.

Surface area is an attractive parameter for emulsion characterization because it has been directly related to the reactivity of the emulsion [1]. However, we found that where the emulsion contained a significant volume of particles below 1 micron, there was considerable variation in the values of the surface area measurements in the four laboratories and we do not know the source of this variation.

The median particle size (i.e. D50) has been used by several authors; it has the advantage of not assuming any particular distribution and is not sensitive to 'outlying' parts of the size distribution. In this study it was found to be the size measurement with the least variation between the four laboratories, with none of the values differing by more than about 0.2 micron. While it is not possible to completely characterize a particle size distribution with a single figure, for the purposes of quality control the median size provides a reproducible measure. The disadvantage is that it is not associated with a measure of the width of the distribution. However, we found that the width, expressed as a ratio of the S.D. to the median, did not differ between the emulsions studied. All the emulsions were prepared with conventional colloid mills. Possibly unconventional emulsification techniques like the Esso SMEP process would give significantly different 'widths' of the size distribution.

It is interesting that nearly all of the emulsions gave peaks or shoulders in the range of 10-20 micron which was reproduced in all the laboratories. This seems to be a real feature of the particle size distribution of the emulsions and may reflect some coalescence on exit of the colloid mill. A similar shoulder was seen by Sainton *et al* who used a microscopic technique for sizing [8].

Conclusions

Particle size measurements made in the same laboratory show a high degree of repeatability and test results such as median particle size, which can be correlated with the field performance of emulsions, can be obtained. Agreement between laboratories is less good, mainly because the problem of sample dispersion and stabilization has not been fully solved, but the median particle sizes obtained were reproducible to ca. 0.15 micron (d2s).

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