PAINT RESEARCH BULLETIN

RC-84

SUBJECT

SOME ASPECTS OF CRITICAL PIGMENT VOLUME RELATIONSHIPS

Prepared by: W. K. Asbeck

April 6, 1948

PAINT RESEARCH DEPARTMENT

CHICAGO, ILLINOIS

Some Aspects of
Critical Pigment Volume Relationships
Paint Research Department
W. K. Asbeck

It is only in the last score of years that the significance of pigment/binder relationship has found widespread recognition in the paint industry.[1] More and more the formulator is making use of the concepts of pigment volume rather than relying on the older methods of formulation purely by weight relationships. It has been determined that substitutions in a paint formulation purely on the weight basis do not fill the expected requirements and it is only within very recent times that the recognition of the value of a more accurate knowledge of pigment/binder relationships has thrown considerable light on the mechanics of paint system substitutions.

PIGMENT-VOLUME-CONCENTRATION

$$\text{P.V.C.} = \frac{(\text{VOLUME OF OPAQUE PIGMENTS + EXTENDERS})}{(\text{VOLUME OF OPAQUE PIGMENTS + EXTENDERS}) + (\text{VOLUME OF NON-VOLATILE VEHICLE SOLIDS})} \times 100$$

EXAMPLE:

$$\text{P.V.C.} = \frac{(10 + 25)}{(10+25) + (65)} \times 100$$

$$= \frac{35}{100} \times 100$$

$$= 35\%$$

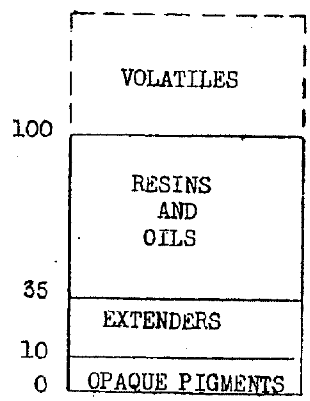


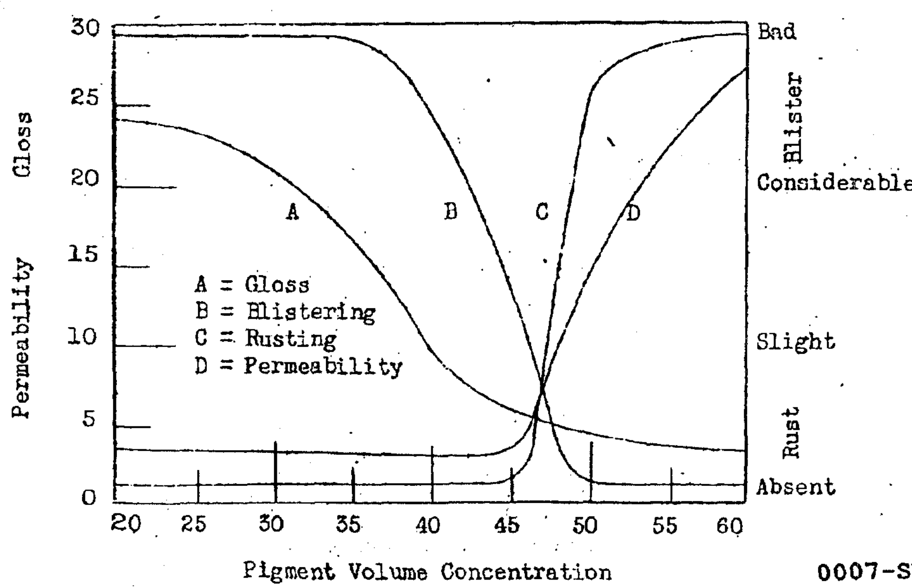
Figure 1

The concept of "pigment volume concentration" has found almost universal acceptance in the paint industry. As illustrated in Figure 1, the pigment volume concentration, or in short PVC of a paint is the volumetric percentage of pigment present in the total solids of a paint system, and excludes all volatiles from the calculation. The PVC then, represents the volumetric percentage of pigments present in the dry paint film after all thinner has volatilized. The amount of thinner present is immaterial from the standpoint of PVC and is mainly present to obtain the proper painting consistency for the paint.

If a series of paints containing the same constituents are made up with increasing values of PVC, ground to the same dispersion, and such factors as moisture permeability, rusting, blistering and gloss determined on the dried samples, the typical results obtained can be represented by the curves of Figure 2.

Figure 2

CPVC



As the figure illustrates, a more or less sharp break occurs in all of the curves at a PVC of about 43% for the specific combination of pigments and binders shown. The permeability of the samples of PVC above 43% rises very sharply, indicating a porous film. The rusting characteristics rise commensurately, the region of PVC's below 43% showing good rust preventive qualities while above this point, the panels failed very rapidly, as might be expected from the permeability data. The blistering, on the other hand, is very bad at low PVC, improving with higher concentrations of pigment. The gloss curve too, runs somewhat parallel to the blistering curve, showing high gloss characteristics for paint films of low PVC and a decrease of gloss with increasing pigment volume concentration.

It is obvious from Figure 2 that the breaks in the permeability, rusting, blistering and gloss curves all occur at a more or less definite point, about 43% PVC for the pigment/binder combination shown. This point can be designated as the critical pigment volume concentration, or in short, CPVC, for the pigment/binder system involved.[2][3][4] The CPVC is the transitional point above or below which substantial differences in the appearance and behavior of a paint film will be encountered. From Figure 2 it is obvious that different characteristics can be imparted to a paint containing the same constituents by formulating above or below the CPVC.

Factors Influencing CPVC

If the CPVC of several series of samples is determined using the same pigment but various binders, it would appear that identical values of CPVC should result. This is not the case! As Figure 3 shows, the permeability curve - which is the more direct means of measuring the pigment volume concentration above which a dried paint film becomes porous - breaks very sharply at a PVC of about 26% in the case of the formulation involving anatase titanium dioxide and raw linseed oil, while the use of the same pigment and bodied linseed oil causes the break in the curve to advance to about 38% PVC. A change in the critical pigment volume concentration of over 10% has taken place by replacing raw linseed oil by bodied linseed oil. If now, a mixture of equal parts of the same raw and bodied linseed oils is used in the formulation involving the same pigment, a value of CPVC practically identical with that of the bodied linseed oil alone results instead of a value lying somewhere between the two as might have been expected. This is brought out graphically in curve "C" of Figure 3.

Moisture Permeability

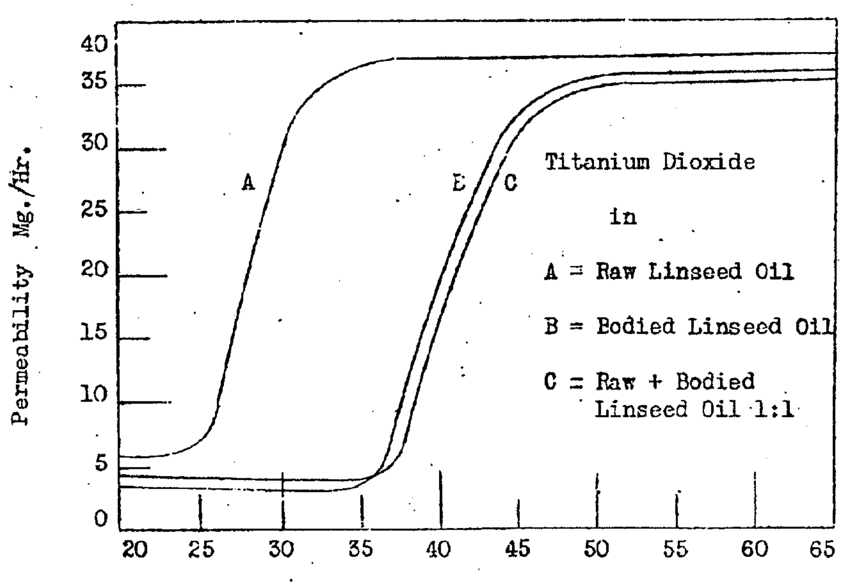
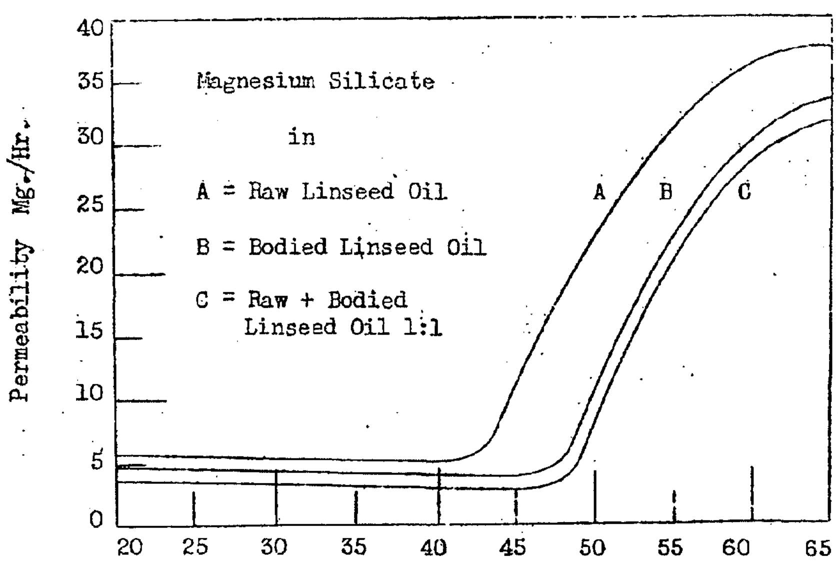


Figure 3

0007-SWP-044726

That this change in CPVC through the use of differing binders is not limited to the use of TiO_2 pigment alone is shown in Figure 4. Here a fibrous magnesium silicate pigment has been used with the same raw and bodied linseed oils and a combination of equal parts of the two as above. A very similar pattern results. The general values of CPVC have, however, advanced to a higher region, namely 41% and 46%, and the differences between the two types of oil have been reduced to about 5%. But here again, the raw linseed oil gives the lower value of CPVC, while the bodied linseed oil and the formulation using the combination of the two lies at substantially the same value as that for the bodied linseed oil alone.

Moisture Permeability



Pigment Volume Concentration

Figure 4

From the above it is apparent that not only the type and general packing characteristics of the pigment, but their physical relationships to various vehicles play a major part in the determination of the critical pigment volume concentration of a pigment/binder system.

That other factors than the above have an influence on CPVC is illustrated in Figure 5. Here, the same anatase TiO_2 pigment as used above is dispersed in a series of binders consisting of increasing amounts of linseed fatty acids in alkali refined linseed oil. Curve "A" represents the moisture permeability of the TiO_2 pigment in alkali refined linseed oil alone, "B" the same with 1% of the fatty acid, "C" 2%, and "D" 5% of the fatty acid present in the dispersion on the basis of pigment volume.

Moisture Permeability

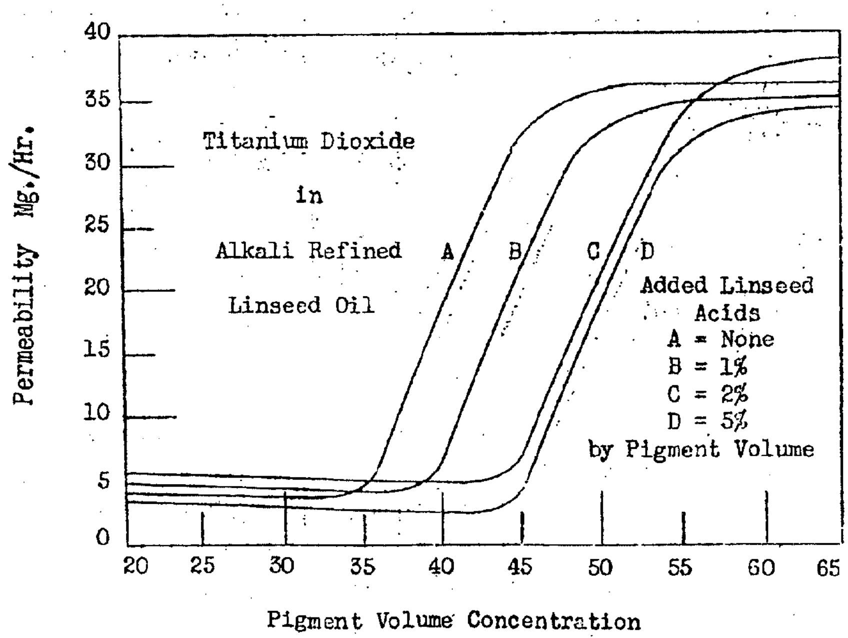


Figure 5

0007-SWP-044728

It is obvious that the CPVC has shifted a total of 7% from 36% CPVC for the combination involving anatase TiO_2 and alkali refined linseed oil alone, to 43% for the samples to which 2% and 5% of the linseed fatty acid have been added. The 1% added linseed fatty acid curve breaks at an intermediate point, namely 39%. Changing the surface characteristics has caused a change in the packing of the pigment particles. It is particularly interesting to note that the breaks in the 2% and 5% curves are practically coincidental, indicating that no additional advantage has been achieved by the addition of more than 2% linseed fatty acid for the pigment/binder system involved.

The explanation for this can probably be most satisfactorily found in the fact that a selective adsorption from solution determination[5] revealed that the titanium dioxide involved in the formulation adsorbed 2.1% of the linseed fatty acid upon its surface. Below this quantity, all the surface requirements of the pigment with regard to the acid are not filled, giving intermediate values of CPVC, while above this, the material is merely in excess; 2.1% being sufficient to completely cover the surface of this pigment.

Another factor found to influence the critical pigment volume concentration was the degree to which the pigment in the paint was dispersed. A poorly ground paint results in a lower CPVC than a well ground one. Figure 6 shows the results obtained by grinding an anatase TiO_2 in bodied linseed oil to various Hegman Grind Gage values. It can be seen that although the differences in CPVC with various grinds are relatively small, a definite progression occurs with increased fineness of grind.

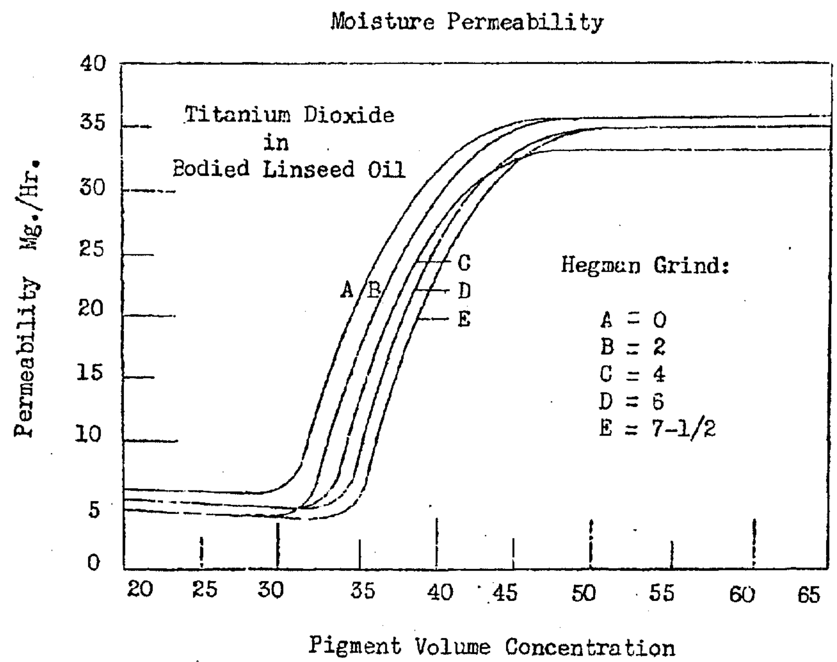


Figure 6

The factors then, influencing the CPVC of a paint system are, among others:

1. The fundamental packing characteristics of the pigment.
2. The type of binder employed.
3. The types and amounts of agents present.
4. The fineness of grind of the system.

CPVC and Dispersion

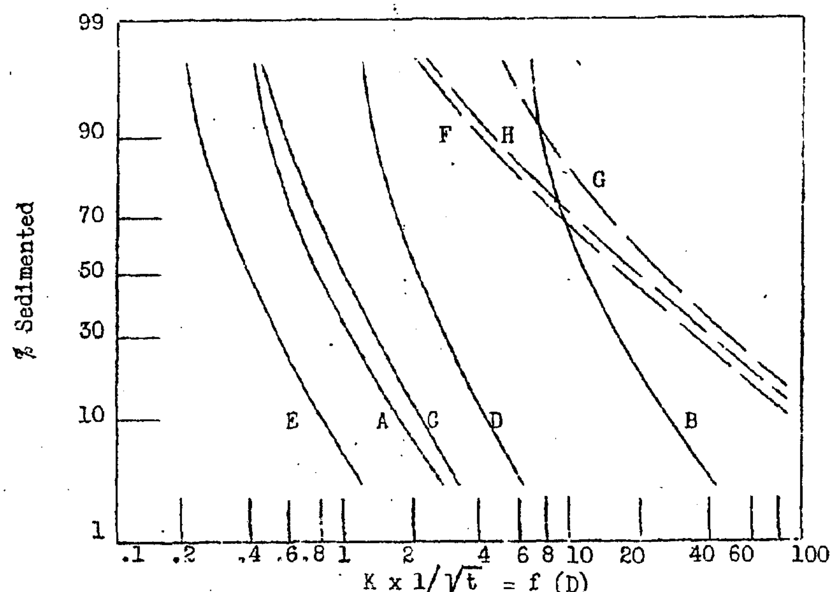
A survey of the above factors seems to yield only one common basis upon which these changes in CPVC can be placed: the degree of dispersion or agglomeration. Another factor supporting this is that an examination of the paints resulting from each of the above combinations of pigments and binders reveals in the case of similar systems, that that system showing the lower CPVC also shows more thixotropic effect while conversely that system with higher CPVC is decidedly "smoother" in its texture. This undoubtedly results from differing degrees of agglomeration or dispersion of the pigments in the various binders involved.

To ascertain the validity of this conclusion, a number of "agglomerate size" determinations were made by one of the well known settling methods.(7) A number of preliminary runs clearly indicated that the pigment particles participating in an individual agglomerate show a decided rigidity and resistance to being dispersed into the liquid medium used as the dilution fluid, particularly if non-polar solvents are employed for this purpose. In the course of the sedimentation investigations, no instance was noted where agglomerated systems showed a tendency to disperse in the solvent liquid, and conversely no dispersed system showed the tendency to agglomerate. It is of course necessary to use solvents compatible with the vehicle employed in the paint.

The sedimentation determination clearly indicated the CPVC of a given system to be a function of the degree of agglomeration or dispersion in which the system exists. A highly disperse system shows high CPVC, a poorly disperse system shows low CPVC in relation to the fundamental packing characteristics of the pigment.

Figure 7

Dispersion



TiO_2 in Linseed Oils
A = Bodied
B = Raw
C = Raw + Bodied 1:1
D = Alkali Refined
E = Alkali Refined + 2% Linseed Acids

Mg Silicate in Linseed Oils
F = Bodied
G = Raw
H = Raw + Bodied 1:1

Figure 7 shows the values obtained for the sedimentation curves of the same anatase TiO_2 in raw linseed oil, bodied linseed oil, alkali refined linseed oil and alkali refined linseed oil with 2% by volume of pigment linseed fatty acids added as well as magnesium silicate in raw and bodied linseed oils. The curves for both of the above pigments dispersed in a mixture of equal parts of raw and bodied linseed oil is also included. The degree of dispersion in both cases, as determined by the sedimentation curves, is almost identical with that of the bodied linseed oils alone. This clearly explains the reason for finding the same values of CPVC for the pigments dispersed in bodied linseed oil alone and in the 1:1 combination: both systems show the same degree of dispersion of the pigment incorporated in them.

The ordinate of Figure 7 represents the weight per cent of pigment sedimented based on a probability scale,[8] while the abscissa carries a logarithmic scale of a function of the reciprocal square root of the sedimentation time. This is proportional to the diameter of the particles.* It was found preferable to use this function rather than the calculated diameter of the agglomerates because of the difficulty of determining the absolute specific gravity of the agglomerates which is included in the factor (d_1-d_2) of Stokes' Law. Because of the oil incorporated in the pores of the agglomerates, the specific gravity will be less than that of the solid pigment particles, so that the factor (d_1-d_2) becomes too large where agglomerated particles are concerned if the density of the solid pigment particles is taken for d_1.

A comparison of Figure 7 with the Figures 3, 4 and 5 clearly shows the direct relationship between increased agglomerate size and decreased CPVC.

*Footnote:

The basis for this calculation is Stokes' Law, which states:

$$D = \sqrt{\frac{9\,h\,\eta}{2t\,(d_1-d_2)g}} = K \times 1/\sqrt{t}$$

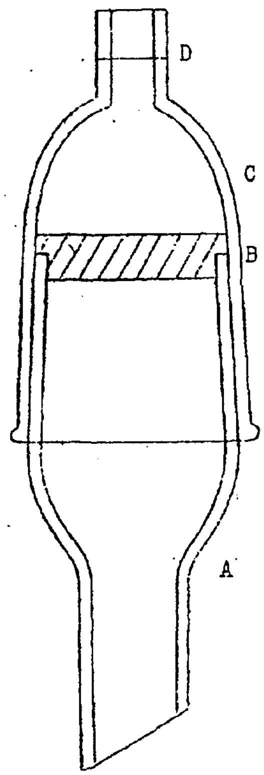
Where: D = diameter of particles; h = distance of fall; t = time of fall; η = viscosity of liquid; d_1 and d_2 = specific gravity of solid and liquid; g = gravity constant.

The Critical Pigment Volume Concentration Cell

A clear understanding of the intrinsic dependency of CPVC upon the relative degree of dispersion or agglomeration leads to the conclusion that the critical pigment volume concentration is determined by the packing characteristics of the pigment particles in relation to the binder employed in the system. The CPVC is that point in a pigment/vehicle system at which just sufficient binder is present to completely fill the voids left between the pigment particles incorporated in the film after volatilization of all thinner. It represents the densest packing of the pigment particles commensurate with the degree of dispersion of the system.

If the above conclusions are correct, and the agglomerates possess the rigidity indicated in the sedimentation determinations, a packing system of pigments commensurate with that obtained in a dried paint film should be produceable by other methods. One of the most obvious and simple ways would be to measure the volume of a pigment paste cake after all excess liquid has been removed by filtration. By determining the ratio of the volume of this cake to the true volume of the pigment present as determined from the formulation of the original dispersion or other appropriate method, a value commensurate with the CPVC should result.

The CPVC cell, as developed in this laboratory, consists, as Figure 8 illustrates, of a standard ground glass joint to the top portion of the male section "A" of which a glass or metal fritted porous plate "B" has been firmly attached. The female section is constricted shortly above the ground glass portion to a narrow opening around which a calibration mark "D" has been placed.



CPVC - Cell

Figure 8

The method of making a determination consists of diluting the paint to be tested in equal part with a high boiling naphtha or other suitable solvent and transferring a measured volume of this into the top of the CPVC cell by means of a calibrated syringe. A vacuum is applied to the bottom of the cell and all excess liquid filtered out. The filtration can easily be observed through the glass walls of the cell. After all excess liquid has been removed, the vacuum is broken and the cell filled to the calibration mark with a measured volume of water introduced from a burette or measuring pipette. Knowing the total volume of the cell from a previous calibration, the difference between the total volume and the measured volume represents the volume of the filter cake, including all voids.

The results obtained by this method check excellently with the values obtained by the permeability-draw down method, indicating that the conclusions concerning the packing characteristics at the CPVC are correct. The mean difference between the two methods runs about ± 2%, well within the limits of experimental error. Some of the results as applicable to this discussion are shown below in Table I.

Table I

	CPVC	
Titanium Dioxide in:	Draw-down	Cell
Raw Linseed Oil	26%	27%
Bodied Linseed Oil	38%	38%
Raw + Bodied Linseed Oil	39%	38%
Alkali Refined Linseed Oil	36%	35%
Alkali Refined Linseed Oil + 2% Linseed Fatty Acids	43%	43%
Magnesium Silicate in:		
Raw Linseed Oil	41%	39%
Bodied Linseed Oil	46%	47%
Raw + Bodied Linseed Oil	46%	46%

Pigment/Binder Relationships

The recognition of the physical meaning of CPVC as being that point at which just sufficient binder is present to completely fill the voids left between the particles of a pigment/binder system, leads to a necessary change in the concepts of pigment/binder relationships. Until the present the binder in a paint system has been classified into two general types, namely the "bound" oil and "free" oil. The bound oil has generally been considered to consist of an envelope of molecules firmly adsorbed to the surface of the pigment particles from the vehicle and may, physically, be identified with the pigment. These molecules of binder are removed from the surface of the pigment only through considerable effort and can consequently be regarded as being truly "bound" to the pigment by strong physico-chemical forces. The quantity of such binder firmly adsorbed to the solid particles can vary between low values of less than 1% to well above 10% of pigment volume, depending upon the type of vehicle employed in the system and the surface characteristics and area of the pigments. Some typical values are: anatase TiO_2 in raw linseed oil - 2.5%; in bodied linseed oil - 4.8%; in alkyd varnish - 10.3%; magnesium silicate in raw linseed oil- 2.0%; in bodied linseed oil - 3.1%; in alkyd varnish - 5.0% of oil, by pigment volume adsorbed.

The free binder has been considered to be all the rest of the oil present in the paint system at the formulated PVC. It is that oil which is easily removable from the system in the wet state by such simple methods as filtration and can consequently be regarded as being truly "free."

With the concept of CPVC this "free" portion of the binder must be subdivided into two major parts, namely I, that portion which is required to fill the interstices between the pigment particles when these are at their densest degree of packing commensurate with their dispersion and II, that portion of the binder which is in excess of this amount to the formulated PVC. The first of this oil can be regarded as being "interstitial" binder, and the second as "excess" binder.

These relationships can probably be most adequately represented by Figure 9.

Pigment/Binder Relationships

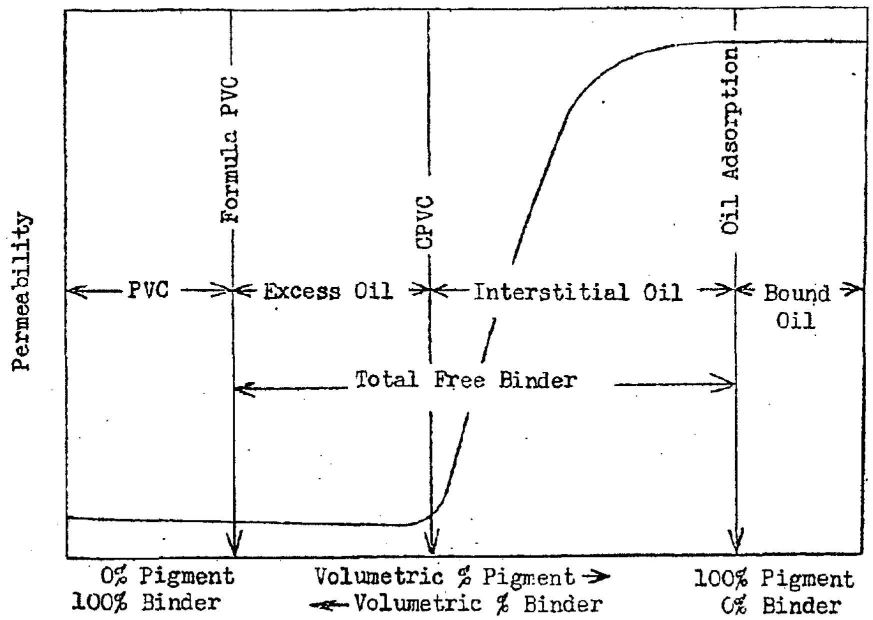


Figure 9

If a permeability vs. PVC curve is determined for a given pigment/binder system, the results can be represented by a typical graph as in Figure 9 and as previously described in Figures 3, 4 and 5. The sharp break in the permeability represents the CPVC, or that ratio of pigment to total solids where just sufficient binder is present to give a continuous solid/liquid phase after all thinner has volatilized. The PVC of the paint is determined by the formulation, while the bound oil can be evaluated by an adsorption determination. Mathematically, the system can be defined by the simple relation:

Total Volume = PVC + Excess Oil + Interstitial Oil + Bound Oil

and: Excess Oil + Interstitial Oil = Total Free Binder

Where agglomerated systems are encountered as for instance is the pronounced case for TiO_2 in raw linseed oil, it is necessary to subdivide the interstitial binder into two further groups, namely: 1. intra-agglomerate oil, and 2. extra-agglomerate oil. The first represents that binder which is present inside the pores of the individual agglomerates, while the second is that which fills the spaces between them, or:

Interstitial Oil = Intra-Agglomerate Oil + Extra-Agglomerate Oil.

An evaluation of these two terms can be made with the assumption that the particles participating in an agglomerate are at their densest degree of packing. Consequently, in an isolated agglomerate the same pigment/vehicle ratio would exist as is obtained by a CPVC determination on a mono-disperse system of the same pigment. The arithmetical difference between the CPVC of the mono-disperse system and that of the agglomerated system then represents the extra-agglomerate oil, and the difference between this and the interstitial oil is the intra-agglomerate oil. These relations are represented in graphical form in Figure 10, where the remainder of the values conform to those of Figure 9.

From Figure 10, it can easily be perceived that the extra-agglomerate oil represents the difference in efficiency of packing between an agglomerated and a completely dispersed pigment system. For the latter, the intra-agglomerate oil simultaneously represents the interstitial binder.

A consideration of these factors immediately raises the question, "Which portion of the vehicle is responsible for the wide divergence of pigment packing behavior?" By the use of various vehicles and agents the same pigment system can be induced to give high or low values of CPVC, Pigment/Binder Relationships

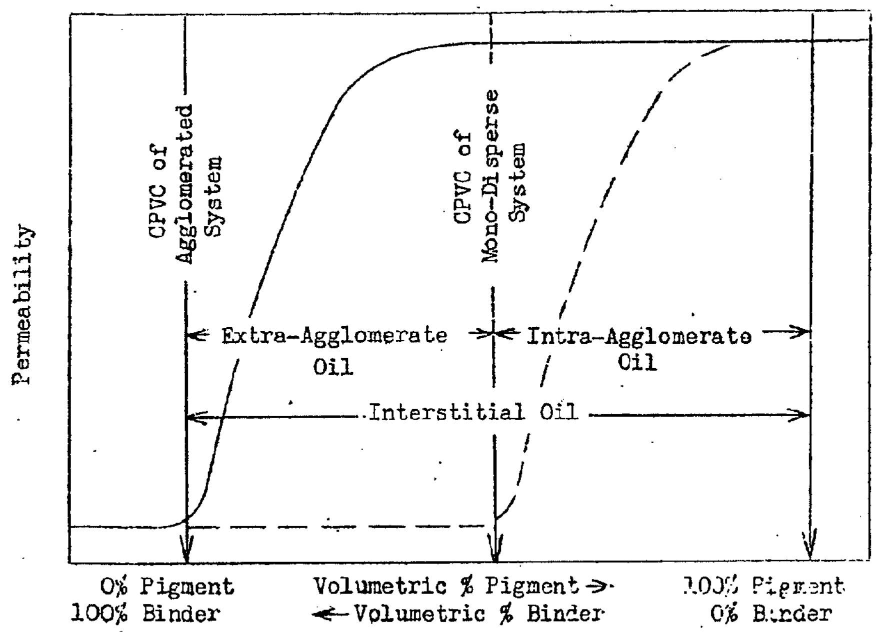


Figure 10

The answer can readily be found through the use of the CPVC cell. It is possible to c ompletely substitute the total free binder of a paint system by a solvent and still retain the same packing characteristics as characterize the original paint. The interstitial binder and excess binder consequently must be considered to play only a minor role in the establishment of the CPVC, while the bound oil is the main factor in determining this value.

The vehicle substitutions were carried out by diluting the original paint in equal part by volume with naphtha or other suitable solvent and centrifuging out the pigment. The supernatant liquid is decanted and replaced with the same volume of solvent. The pigment is then redispersed into the solvent by rigorous shaking, and repetitions of this whole procedure made until only traces of binder can be detected in the solutions. A CPVC determination, by means of the CPVC cell, is then carried out on this dispersion, while another is made on the original paint. The results obtained by these two methods check well within experimental error for systems exhibiting both highly agglomerated as well as highly dispersed states.

That the adsorbed or bound oil is not removed from the surface of pigment particles by simple dilution of this type has been pointed out by previous authors,[5] and has been further corroborated in the course of this investigation.

Conclusions

1. The CPVC (Critical Pigment Volume Concentration) of a paint system is the transitional point above or below which substantial differences in the appearance and behavior of a paint film will be encountered. It is that point in a pigment/vehicle system at which just sufficient binder is present to completely fill the voids left between the pigment particles incorporated in the film after volatilization of thinner. It represents the densest degree of packing of the pigment particles commensurate with the degree of the dispersion of the system.

2. The CPVC is influenced, among other factors, by:

   a. The fundamental packing characteristics of the pigment or combination of pigments involved.

   b. The type of binder employed.

   c. The types and amounts of special agents present.

   d. The fineness of grind of the system.

3. The CPVC is determined by the degree of dispersion of the pigment in the binder in combination with the fundamental packing characteristics of the pigment particles. An agglomerated system of pigments shows low CPVC while a highly dispersed system of the same pigments shows high CPVC.

4. In the concepts of pigment/binder relationships a number of new terms have been introduced to characterize the physical relations between pigments and vehicles. The Bound Oil is that portion of the vehicle firmly adsorbed to the surface of the pigments. The Interstitial Oil is that portion of the binder required to fill the interstices between the pigment particles when these are at their densest degree of packing commensurate with their dispersion. The Excess Oil is that portion of the binder in excess of the Interstitial Oil plus the Bound Oil.

In agglomerated systems, the Interstitial Oil is subdivided into two further parts. The Intra-Agglomerate Oil is that portion of the binder present inside the individual agglomerates. The Extra-Agglomerate Oil is that portion of the Binder filling the spaces between the agglomerates when these are close packed.

5. The Bound Oil of a paint system characterizes the degree of agglomeration or dispersion, and consequently the CPVC of the system.

6. A CPVC Cell was developed to determine the CPVC of a paint system on a single sample in the wet state.