

Surface Active Agent Phenomena in Dust Abatement

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This investigation was undertaken because of conflicting reports regarding the effectiveness of surface active agent solutions used as sprays in dust-abatement work, and because of the need for means of relating the activity of various agents in the form of bulk solutions with their activity in the form of sprays.

That dust wetting results determined from bulk solution tests should not be expected to hold in the case of spray droplets was brought out through application of the Gibbs excess concept, after the applicability of this concept to dilute surface active agent solutions had first been verified. Experimental results from a simple dust wetting technique with bulk solution and the surface tension-concentration curve of the agent show how the concentration of agent required to produce dust wetting droplets of varying size can be estimated.

The requisite concentration, hence cost of agent, increases rapidly with decreasing spray droplet size, and may be 10- to 100-fold greater than for dust wetting by bulk solutions.

FOR many years surface active agents have been used in water sprays for the abatement of dust. The principal benefit claimed for their use has been that they enable water to wet the dust more readily—a factor believed to be advantageous in knocking the dust out of the air more quickly. The increased wetting power of a surface active agent-water solution is based not only on the reduction of surface tension of the solution but also upon the reduction of the interfacial tension between the solid and liquid. Despite the theoretical reasons why utilization of a surface active agent (commonly called wetting agent) should improve dust abatement, conflicting reports on their merits have come to the attention of the authors, particularly with reference to dust abatement in coal mines and at coal cleaning plants.

A considerable amount of work has been done on the use of wetting agents for dust abatement, much of which has been reviewed in recent publications by the U. S. Bureau of Mines (11, 13, 21, 24). A recent report by Merritts and Reay (21) deals with the use of wetting agent sprays for abatement of dust during continuous miner operations. They report that up to 90% of the dust present when water alone is used is knocked out of the air when slightly higher than 0.01% wetting agent solutions are employed.

The authors thoroughly investigated a wide variety of promising surface active agents in order to determine the most economical ones in terms of efficiency and cost. The relative merits of these agents were determined by gently dropping coal particles, ranging in equivalent diameter from 25 to 100 microns, individually, onto the surface of solutions of wetting agents of various concentrations contained in 250-ml. beakers.

Preliminary tests were made with 16 size fractions separated from a bituminous coal sample. These fractions had equivalent

diameters ranging progressively from 25 to 44 microns up to 840 to 1000 microns. Results indicated that, for the procedure employed, the rate of disappearance was not a measurable function of particle size. For the standard test, therefore, the procedure adopted consisted of dropping coal particles, individually, approximately 1 cm. onto the surfaces of progressively more dilute solutions until a dilution was found at which the particles were not instantaneously wetted. For Tergitol this concentration was found to lie between 0.0030 and 0.0025 weight %.

The time of wetting was measured as the time for the particles to disappear from the surface of the solution. This test was adapted from the widely used Draves test (5, 6) for the wetting of fabrics. If the time of wetting of the coal particles was virtually instantaneous, the agent was classified as satisfactory.

The various agents were tested in distilled water and in the presence of acids, bases, and salts apt to be found in typical mine waters. Although the data herein reported are for distilled water solutions, the particular agent used was found equally effective in the typical mine water solutions.

In this way a wide variety of surface active agents was evaluated on a relative basis, even though specific data could not be secured regarding the effective concentrations necessary when the agents were used in sprays.

SURFACE ACTIVE AGENT PHENOMENA

To comprehend more clearly the possible implications of laboratory wetting results and to permit use of such data in specific spray application problems, a study was made of the phenomena of surface active agent solutions and the physical changes involved in going from large volume solutions to small droplets. From this study, it would appear possible to use wetting results obtained with large volume, dilute or bulk solutions, to predict wetting with spray droplets, if it is realized that in spray droplets the ratio of the surface area to volume is much greater

than for bulk solutions. For example, the average bulk solution used in laboratory tests had a volume of 200 ml. and a total liquid-glass plus liquid-air interface of roughly 20 sq. cm. or a surface to volume ratio of 1 to 10. On the other hand, for a spherical droplet the ratio of surface to volume is $6/d$, or for droplets 20 microns (2×10^{-3} cm.) in diameter the ratio is 3000 to 1. This means that for 20-micron droplets, a size commonly found in liquid sprays, the surface to volume ratio is about 30,000 times as great as for bulk solutions. Consequently, it is necessary to take into account surface phenomena that will alter the wetting behavior of similar initial concentrations of solutions in droplets compared to bulk volumes.

GIBBS EXCESS. An important tool that can be used to study the surface phase of wetting agent solutions is the thermodynamic principle postulated by J. Willard Gibbs that in any surface active agent solution the wetting agent diffuses to the surface to produce a film that contains a large concentration excess of the active agent over that which exists in the main bulk solution. Using rigorous thermodynamics, Gibbs then derived a workable equation [a derivation of which is available in any standard text (9) on chemical thermodynamics] to enable one to calculate this excess. This equation can be written in the form

$$\Gamma = -(1/RT) (d\gamma/d \ln a) \quad (1)$$

where

Γ = Gibbs excess in moles of surface active agent per unit of surface area above concentration that would normally be in the surface film owing to bulk concentration, moles per square centimeter

R = gas constant, 8.31×10^7 ergs per ($^{\circ}$ K.) (gram mole)

T = temperature of the solution, $^{\circ}$ K.

γ = surface tension of the solution, dynes per centimeter

a = bulk activity of the surface active agent, dimensionless

For very dilute solutions such as herein discussed the activity of the solute can be safely replaced by its concentration. Therefore, it may be seen that if the surface tension versus the log of the concentration of the solution is plotted, the Gibbs excess can be determined at any concentration of active agent solution from the slope of the plot at that point.

NATURE OF SURFACE FILM OF WETTING AGENT SOLUTION. Before using the Gibbs excess to predict from laboratory data on bulk solutions the ability of spray droplets to wet coal, it is of interest to examine the nature of the surface film of wetting agent solutions more thoroughly.

From studies on the films of insoluble substances upon water, Langmuir (14-18) concluded that films of high molecular weight acids and alcohols are unimolecular. Furthermore, he concluded that the molecules in the film were definitely oriented in a vertical plane with the nonpolar part of the molecule forming the apparent surface and the polar part of the molecule attracted to the bulk water layer. These conclusions suggest that the Gibbs layer or film is but one molecule thick, and it is evidently important to consider how far one is justified in making the assumption that in all cases, both for pure liquids and for solutions, the Gibbs layer may be considered as similar in character—that is, unimolecular in thickness and consisting of oriented or partially oriented molecules.

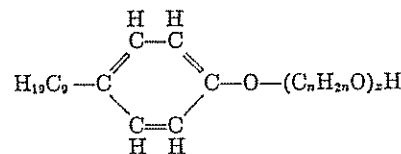
In the case of insoluble oil films, the experimental verification is comparatively simple. When a known weight of oil is placed on a trough of absolutely clean, grease-free water, the oil spreads out quickly to form an extremely thin layer; and when the film has completely spread, its area can be determined. Thereupon, the average cross section of the surface active molecule and the thickness of the film can be calculated, assuming that the surface film has a thickness of one molecule of agent, oriented vertically in the surface. The length and cross section of the molecules calculated in this way are in excellent agreement with the values obtained from molecular bond distance calculations, thereby indicating the existence of the assumed unimolecular layer.

The explanation of this vertical alignment of insoluble molecules at the interface has been offered by Harkins (10) and Langmuir (14) among others. Higher alcohols and fatty acids have a polar and nonpolar portion. There is a strong dipole attraction between the polar portion of the molecule and the water molecule but little attraction between the hydrocarbon portion of the molecule and water. As a consequence, in the surface the polar end of the molecule is drawn into the water and the nonpolar portion is not. The result is that the molecules become oriented with their "heads" attached to the water and their "tails" aligned vertically in the surface.

In the case of soluble surface active agents it is not possible to determine the orientation and thickness of the surface layer directly. However, an indirect approach is possible by comparing the amount of agent that would theoretically be present in a unimolecular vertically oriented layer, with the amount calculated to be present in the actual layer from Gibbs excess data. If the two values agree, the conclusion may be accepted that with the soluble surface active agent in question, the molecules are present in an oriented unimolecular layer.

Tergitol dispersant NPG (hereinafter designated as Tergitol), manufactured by Union Carbide & Carbon Corp., is used to illustrate the theory because considerable data are available on this agent. The same reasoning can be applied to any other agent, however, provided the necessary data are available.

THEORETICAL QUANTITY OF AGENT IN ORIENTED UNIMOLECULAR LAYER. According to the manufacturer, Tergitol is a non-ionic surfactant and a blend of several members of a homologous series, having the formula:



where x in the average case is 10 and the oxide is approximately an equal mixture of ethylene ($n = 2$) and propylene ($n = 3$). The density is 1.052 at 20° C. The average molecular weight of the polymer is 715. The C_x portion of the molecule is nonpolar—that is, repelled by water—and the oxide part of the molecule is water-"loving." By use of molecular bond distances and angles (8, 25), it is possible to calculate the approximate average length of the Tergitol molecule. Since the polymer is a mixture of the ethylene and propylene oxide types, the average length can be taken approximately as the mean between the two molecular lengths or 55 Å. (55×10^{-8} cm.). From the length, molecular weight, and density, the effective cross-sectional area occupied by one molecule of Tergitol oriented vertically in the surface can be shown to be 20.6 sq. Å. (20.6×10^{-16} sq. cm.).

This area is in striking agreement with the effective displacement surface area (20.5 sq. Å.) found by numerous investigators (1-3, 19, 22, 25) for insoluble aliphatic single chained compounds on water. In the case of insoluble liquids, the displacement area of 20.5 sq. Å. is in excellent agreement with values obtained independently by x-ray analysis and is claimed as an indication of close packing in the surface layer.

Since there are 6.02×10^{23} molecules per gram mole, the gram moles per square centimeter of surface should be 8.3×10^{-10} at maximum packing for pure Tergitol.

CALCULATED QUANTITY OF AGENT FROM GIBBS EXCESS. The surface tension of Tergitol was determined over a wide range of concentrations using the standard Cenco precision du Noüy tensiometer. The solutions were held at $20^{\circ} \pm 0.2^{\circ}$ C., five simultaneous readings made at each concentration, and the results averaged. In all cases, the five readings were consistent within themselves to ± 0.2 dyne per cm. Before the solutions were read, they were stirred for 0.5 hour to ensure thorough mixing and then allowed to stand for an additional 0.5 hour

before reading. As a check on the sufficiency of the 0.5-hour sitting time several solutions were allowed to stand overnight and then reread. The results indicated no trend over those that had stood for 0.5 hour and the readings could be duplicated within 0.2 dyne per cm. In this case the range of concentration close to the minimum required to wet coal satisfactorily in bulk solutions was of particular interest.

per molecular layer of thickness. Therefore, the 5.3×10^{-10} gram mole per sq. cm. (Figure 2) maximum Gibbs excess represents essentially the maximum moles of Tergitol per square centimeter present in the surface layer.

COMPARISON OF THEORETICAL AND CALCULATED VALUES. For maximum packing and vertical orientation of a unimolecular layer, 8.3×10^{-10} gram mole per sq. cm. could be present whereas

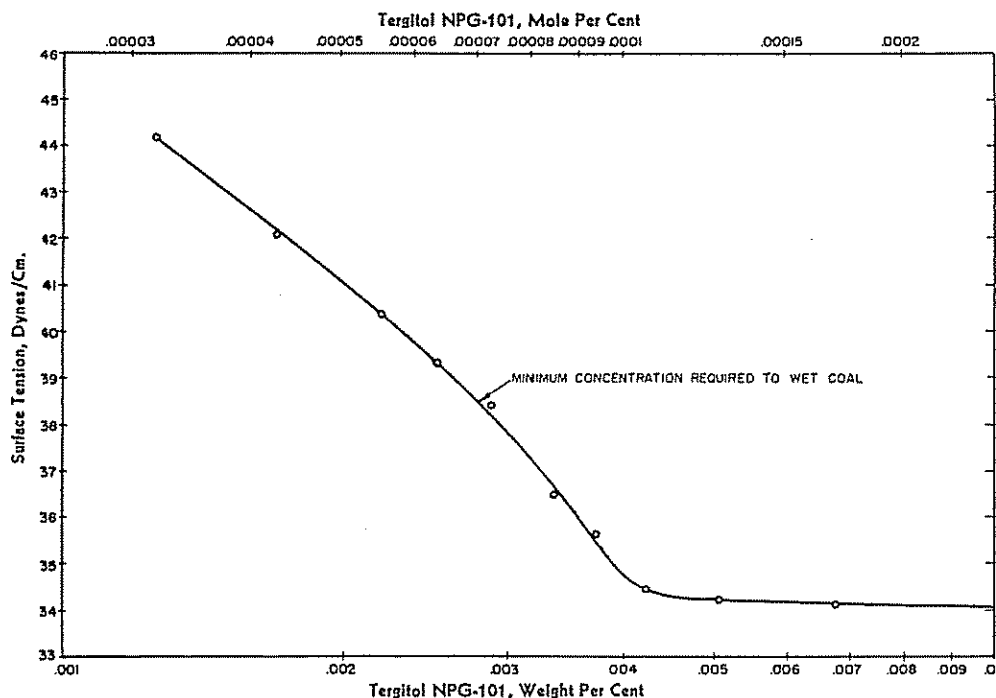


Figure 1. Surface Tension vs. Bulk Concentration
Dilute Tergitol solutions; temperature, 20° C.

Over this concentration range, data were obtained for small concentration changes and the results are shown as a surface tension-concentration plot in Figure 1, together with the minimum coal wetting concentration for bulk solutions. From these data, the Gibbs excess has been calculated and is shown in Figure 2 for the same concentration range. This plot shows the increase of the Gibbs excess with increase in concentration of surface active agent up to a maximum value and then the rapid decrease as the variation of surface tension with increasing concentration becomes extremely small. The very sharp decrease in the Gibbs excess for increasing concentrations past the maximum point is discussed in a later section.

The surface tension-concentration curve indicates the considerable effect a very small amount of the agent has on the surface tension of water. Pure water at 20° C. has a surface tension of 72.8 dynes per cm., yet only 0.005 weight % of the agent added to water lowers the surface tension of the resultant solution to about 34 dynes per cm.—the surface tension of pure Tergitol. The immediate implication is that this very small amount of initial Tergitol is concentrating at the surface as predicted by the Gibbs excess.

It is logical to believe that the surface tension of the solutions should decrease as long as the Tergitol concentration in the surface increases because the pure agent has a much lower surface tension than water. If this is true, it would indicate that the Tergitol concentration in the surface layer at the maximum Gibbs excess concentration of 9.9×10^{-6} mole % is essentially 100 mole % of only a small decrease in surface tension occurs at higher concentrations. It can also be shown that at the maximum Gibbs excess, the contribution of the bulk concentration to the surface layer is negligible—about 2.5×10^{-14} gram mole per sq. cm.

the maximum Gibbs excess calculations indicate 5.3×10^{-10} gram mole. This is remarkably close agreement when it is considered that a slight orientation away from the vertical would decrease the theoretical amount significantly. It also seems highly probable that some water molecules would remain between adjacent Tergitol molecules, at least at the hydrophilic end. Any water remaining in the surface layer would, of course, prevent maximum packing. That the surface layer is essentially unimolecular seems highly probable in view of the agreement between the Gibbs excess and maximum packing calculations. If the 5.3×10^{-10} gram mole in the Gibbs excess layer were distributed throughout more than one molecular layer of depth, the concentration would be proportionally less and the deviation from a pure Tergitol layer proportionally greater in which case one would hardly expect the surface tension of the solution to be equal to that of pure Tergitol.

APPARENT ANOMALY PREDICTED BY GIBBS EXCESS. Reference to Figure 2 shows that after the maximum Gibbs excess is reached, it then drops very rapidly toward zero over the concentration range, 9.9×10^{-6} to 1.5×10^{-4} mole % Tergitol. Since the Gibbs excess contributes almost exclusively to the surface concentration in this region, this implies a very sharp decrease in calculated surface concentration. If surface tension is a function of surface concentration, as is certainly the case, then surface tension should increase in this region. However, this is not the case—the surface tension actually decreases approximately 1 dyne per cm. over this concentration range. It would thus appear that for soluble surface active agents, the Gibbs equation holds only up to that bulk concentration which results in a surface layer composed essentially of the surface active agent. Other anomalies past the maximum value of Gibbs excess have been reported (12).

CONCENTRATION OF WETTING AGENT-WATER SOLUTIONS FOR SPRAYING

Use of the previously calculated Gibbs excess is an essential factor involved in the calculation of the wetting agent concentration required for a given size spray droplet to wet coal. Despite the apparent anomaly at concentrations beyond the minimum necessary to wet coal, the theory is essential to clarification of the

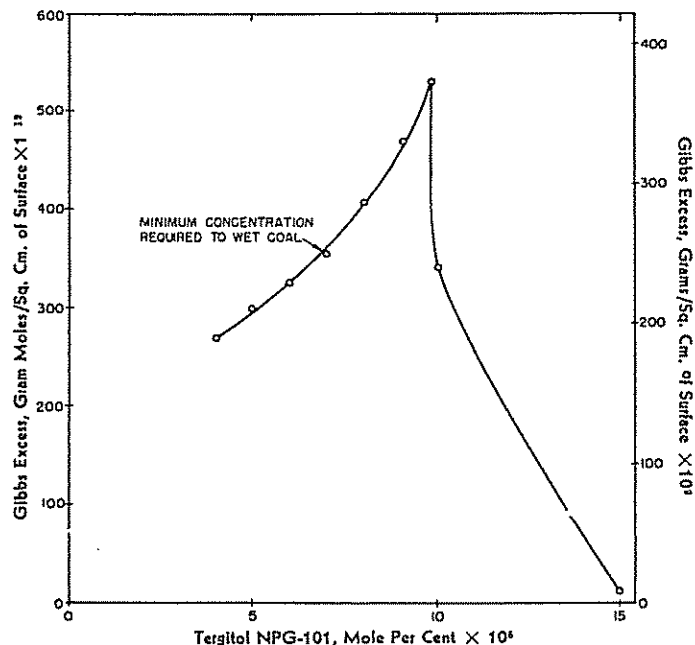


Figure 2. Gibbs Excess vs. Bulk Concentration

procedure involved in the transfer of wetting phenomena from bulk solutions to droplets. Therefore, it is used in the following calculation in the belief that it is the best approach to the problem currently available, but may have to be modified at some future date if the conclusions are inconsistent with new experimental or theoretical evidence.

In the present state of knowledge regarding dust abatement with sprays, it is impossible to state with certainty the optimum size droplet desired to wet a given dust. Droplet size depends upon the spray nozzle used, the pressure at the nozzle (27), the presence of surface active agents, and the condition of the air. For instance, the larger the opening in the nozzle, other factors being equal, the larger the mean droplet size for any given flow rate and hence the less important the small droplets become, since their number decreases. Likewise, the wet and dry bulb temperature determines whether a droplet of a certain size will evaporate and if so how quickly (20). Nevertheless, on a count basis a mean droplet size of about 20 microns is typical of the sprays used in most dust abatement work.

From the curve for the surface tension versus concentration of wetting agent, the amount of agent adsorbed at the surface can be calculated using the Gibbs adsorption equation. Also, for any sized droplet, the resultant interior concentration, after it has been depleted to supply the Gibbs excess, can be calculated if the initial bulk concentration of the droplet at the time of its formation is known. Experiments have shown for Tergitol that, if the bulk concentration is less than 0.0028 weight %, the resultant solution will not wet coal satisfactorily. This

value was obtained from tests in containers holding at least 200 ml. of solution where the adsorption of Tergitol into the surface did not significantly lower the starting solution concentration. However, in small droplets where the surface volume is such a substantial part of the bulk, adsorption to the surface depletes the agent concentration in the interior of the droplet. In the case of droplets where an appreciable difference exists between the starting liquid concentration from which they are formed and the resultant bulk concentration, it is necessary to be able to calculate the final bulk droplet concentration. This final concentration will be a function of the droplet size formed and will determine the final concentration of the active agent in the surface film, which in turn determines the surface tension of the drop and its ability to wet coal. In the following calculation, any effect of the surface curvature of the droplet on the Gibbs excess is assumed to be negligible. Also, the adjustment of the surface film to the Gibbs excess concentration after drop formation is considered to be practically instantaneous. It is realized that in large bulk solutions this is not true (7, 26), but in extremely small droplets with short diffusing distances the Gibbs equilibrium condition is thought to be very rapid.

Based on these assumptions and using Tergitol as the example, the minimum droplet size that will wet coal may be calculated as a function of initial concentration as follows:

$$C_f = C_i - \frac{\text{grams adsorbed in surface}}{\text{grams water in droplet}} \quad (2)$$

where

C_f = final wetting agent concentration in interior of the droplet in weight fraction

C_i = initial Tergitol bulk concentration immediately up/drop formation in weight fraction

Since the grams of water substantially equal the volume of

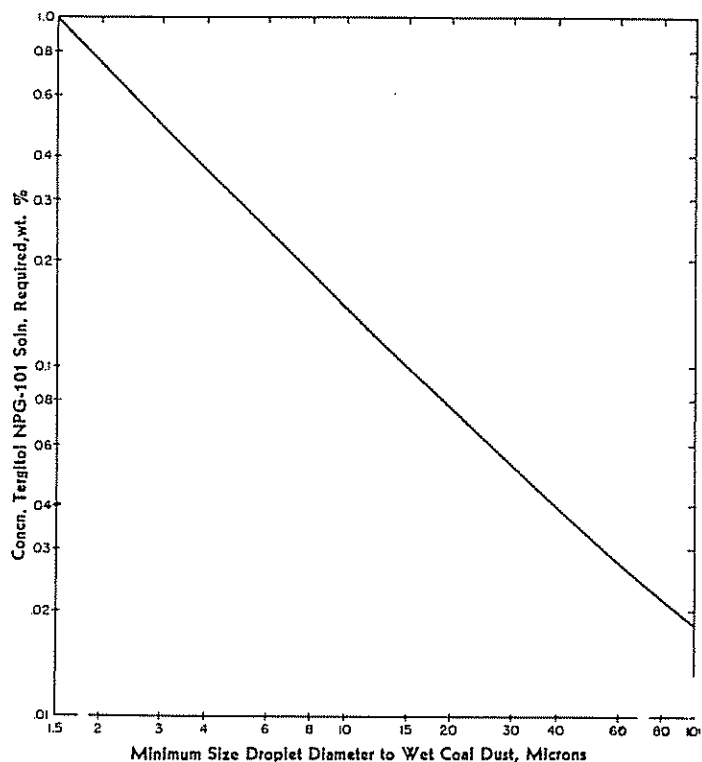


Figure 3. Bulk Concentration vs. Spray Droplet Size

water in milliliters, the equation may be written

$$C_f = C_i - \frac{\text{grams adsorbed in surface}}{\frac{\pi d^2}{6}} \quad (3)$$

where d = drop diameter in centimeters

The grams of Tergitol adsorbed in the surface at C_f equals $(\Gamma_f)(\pi d^2)$ under equilibrium conditions. Γ_f now has the units of grams of Tergitol per square centimeter of surface. Therefore

$$C_f = C_i - \frac{\Gamma_f \pi d^2}{0.52d^3} \quad (4)$$

or converting the diameter to microns and rearranging terms

$$C_i = C_f + \frac{6.0 \times 10^4 \Gamma_f}{d_m} \quad (5)$$

For Tergitol, C_f must not fall below 0.000028 weight fraction if coal is to be wet satisfactorily. Similarly, Γ_f must not fall below its equilibrium value at C_f of 2.5×10^{-7} grams of Tergitol per sq. cm. of surface (Figure 2) if the coal dust is to be wet. Therefore, assuming instantaneous adjustment to the Gibbs excess concentration and substituting the value of Γ_f in Equation 5, it is seen that

$$C_i = 2.8 \times 10^{-5} + \frac{1.5 \times 10^{-2}}{d_m} \quad (6)$$

Based upon this equation, the initial concentrations of Tergitol for various minimum size droplets have been calculated and are shown in Figure 3.

The initial Tergitol solution concentration required to wet coal for spray droplets under 100 microns is much greater than that for satisfactory wetting of coal in bulk solution. Since most spray nozzles now in use give, on a count basis, a mean diameter of spray droplets around 20 microns, the necessity of starting with a relatively high concentration of wetting agent solution is important if the dust is to be wetted in suspension. The large increase in concentration required has a profound effect on the cost of using wetting agents in spraying and, furthermore, probably explains the inconsistent dust abatement results obtained by different workers using surface active agent spray solutions.

ACTION OF WETTING AGENTS IN DUST ABATEMENT

The mechanism by which sprays effect a reduction in dust concentration is still open to considerable question. The following mechanisms have been suggested:

1. Mechanical impingement of spray droplet and dust particle with envelopment of the dust particle
2. Supersaturation of the atmosphere around the dust particle with condensation of the vapor on the dust particle which acts as a condensation nucleus
3. Electrical attraction of dust and spray droplets

In using surface active agents, it is generally assumed that mechanism 1 applies and that the agent permits the dust particle to be wetted more readily; hence a greater number of collisions between dust and spray droplets result in envelopment of the dust particles than if water alone is used.

There are, however, two other possible explanations for the effectiveness of wetting agents in certain cases. First, the

wetting agent will change the size distribution pattern of the spray droplets, other factors remaining constant. Thus, in general, better atomization will be obtained under a fixed set of conditions with wetting agent than without. Second, when sprays are used in coal cutting operations such as the continuous miner, the spray tends to wet the surrounding coal face with a film of wetting agent. In this film, the surface to volume ratio is much less than in the case of spray droplets and the effective coal wetting concentration more nearly approaches that of bulk solutions. At the same time the high pressure sprays create a mass flow of dust-laden air toward the face where the dust may be trapped by the dust wetting film.

Undoubtedly some direct envelopment of dust by spray droplets does occur due to mechanical impact, but it appears highly improbable, in the light of the results presented in the preceding section, that wetting agents in the concentration normally employed have any significant effect upon this phase of dust removal. Similarly, although wetting agents can improve atomization, the same effect can generally be attained by increasing the spray pressure. It would appear, therefore, that the principal advantage of the use of wetting agents may be that of providing a coal dust wetting surface at the face which can trap the dust.

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