FINAL REPORT

PROJECT NO. 186-130

INVESTIGATION OF AGGREGATION OF FINE PARTICLE MATTER SUSPENDED IN AIR

By

J. M. DALLAVALLE,
CLYDE ORR, JR. AND B. L. HINKLE

- o - o - o - o -

CONTRACT NO. DA-18-061-CML-490

CHEMICAL CORPS—CAMP DETRICK
FREDERICK, MARYLAND

- o - o - o - o -

JUNE 14, 1953
FINAL REPORT

PROJECT NO. 186-130

INVESTIGATION OF AGGREGATION
OF
FINE PARTICLE MATTER
SUSPENDED IN AIR

By

J. M. DALLAVALLE,
CLYDE ORR, JR. AND B. L. HINKLE

- o - o - o - o -

CONTRACT NO. DA-18-064-CML-490

CHEMICAL CORPS--CAMP DETRICK
FREDERICK, MARYLAND

- o - o - o - o -

JUNE 14, 1953
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>SUMMARY</td>
<td>1</td>
</tr>
<tr>
<td>II.</td>
<td>INTRODUCTION</td>
<td>4</td>
</tr>
<tr>
<td>III.</td>
<td>THEORETICAL CONSIDERATIONS.</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>A. Mass Decrease with Time</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>B. Number Decrease with Time</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>1. Surface Losses</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2. Aggregation</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>a. Brownian Motion</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>b. Polydispersity</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>c. Van der Waals Forces</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>d. Electric Charge</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>e. Turbulence and Gravity Settling</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>3. Combined Surface and Aggregation Losses</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>4. Dilution</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>C. Effect of Vapors</td>
<td>17</td>
</tr>
<tr>
<td>IV.</td>
<td>EXPERIMENTAL INVESTIGATIONS</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>A. Aerosol Generation</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>B. Aerosol Electrification</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>1. Evaluation</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>a. Apparatus</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>b. Procedure</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>c. Results</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>2. Alteration</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>a. Apparatus</td>
<td>40</td>
</tr>
</tbody>
</table>

(Continued)
TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Corona Discharge</td>
<td>40</td>
</tr>
<tr>
<td>(2) Friction</td>
<td>40</td>
</tr>
<tr>
<td>(3) Radioactivity</td>
<td>40</td>
</tr>
<tr>
<td>b. Effect of Vapors</td>
<td>41</td>
</tr>
<tr>
<td>c. Results</td>
<td>41</td>
</tr>
<tr>
<td>C. Aerosol Aggregation</td>
<td>42</td>
</tr>
<tr>
<td>1. Sedimentation Technique</td>
<td>42</td>
</tr>
<tr>
<td>a. Apparatus</td>
<td>42</td>
</tr>
<tr>
<td>b. Procedure</td>
<td>43</td>
</tr>
<tr>
<td>c. Methods of Analysis</td>
<td>44</td>
</tr>
<tr>
<td>d. Results</td>
<td>45</td>
</tr>
<tr>
<td>2. Dynamic Technique</td>
<td>49</td>
</tr>
<tr>
<td>a. Apparatus</td>
<td>49</td>
</tr>
<tr>
<td>b. Procedure</td>
<td>56</td>
</tr>
<tr>
<td>c. Results</td>
<td>57</td>
</tr>
<tr>
<td>3. Counting Technique</td>
<td>62</td>
</tr>
<tr>
<td>a. Apparatus</td>
<td>62</td>
</tr>
<tr>
<td>b. Procedure</td>
<td>66</td>
</tr>
<tr>
<td>c. Results</td>
<td>69</td>
</tr>
<tr>
<td>V. DISCUSSION OF RESULTS</td>
<td>74</td>
</tr>
<tr>
<td>A. Aerosol Generation</td>
<td>74</td>
</tr>
<tr>
<td>1. Electrical Charge</td>
<td>74</td>
</tr>
<tr>
<td>2. Dispersity</td>
<td>75</td>
</tr>
<tr>
<td>3. Relation of Charge and Frictional Effects</td>
<td>76</td>
</tr>
</tbody>
</table>

(Continued)
VI. CONCLUSIONS

C. Aerosol Aggregation

1. Evaluation

1. Sedimentation Technique

2. Alteration

2. Dynamic Technique

3. Counting Studies

LIST OF FIGURES

1. Aerosol Charge Analyzer ........................................... 22
2. Diagram of Aerosol Charge Analyzer ............................. 23
3. Aerosol Inlet Tube .................................................. 25
4. Circuit Diagram of High Voltage Supply ......................... 27
5. Behavior of a Tobacco Smoke Passing Through No Electrical Field (Upper Block) and Passing Through a Gradient of 5,000 volts/cm. (Lower Block) .................................................. 29
6. Distribution of the Charges on Tobacco Smoke Particles .... 30
7. The Sedimentation of Charged and Uncharged Ammonium Chloride Particles .................................................. 46
8. Photographs of Aggregated Ammonium Chloride Particles .... 47
9. Comparison of the Number of Particles Comprising an Aggregate for Uncharged and Charged Ammonium Chloride Aerosols .... 48
### LIST OF FIGURES (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.</td>
<td>The Sedimentation of an Ammonium Chloride Aerosol in Various Atmospheres.</td>
<td>50</td>
</tr>
<tr>
<td>11.</td>
<td>The Sedimentation of a Magnesium Oxide Aerosol in Various Atmospheres.</td>
<td>51</td>
</tr>
<tr>
<td>12.</td>
<td>Magnesium Oxide Particles Obtained by Sedimentation from Various Atmospheres and After Various Intervals of Time</td>
<td>52</td>
</tr>
<tr>
<td>13.</td>
<td>Ammonium Chloride Particles Obtained by Sedimentation from an Atmosphere of 50 Per Cent Relative Humidity After Various Intervals of Time</td>
<td>53</td>
</tr>
<tr>
<td>14.</td>
<td>Schematic Diagram of Aerosol Apparatus</td>
<td>55</td>
</tr>
<tr>
<td>15.</td>
<td>The Effects of Water Vapor on Light Scattered from Ammonium Chloride Aerosols.</td>
<td>58</td>
</tr>
<tr>
<td>16.</td>
<td>The Effects of Organic Vapors on Light Scattered from Ammonium Chloride Aerosols</td>
<td>59</td>
</tr>
<tr>
<td>17.</td>
<td>Aerosol-Counting Chamber</td>
<td>63</td>
</tr>
<tr>
<td>18.</td>
<td>Circuit Diagram of Scaler Unit and Preamplifier</td>
<td>65</td>
</tr>
<tr>
<td>19.</td>
<td>Aerosol-Counting Apparatus and Auxiliary Equipment</td>
<td>68</td>
</tr>
<tr>
<td>20.</td>
<td>Decrease of Particle Number with Dilution</td>
<td>71</td>
</tr>
<tr>
<td>21.</td>
<td>Effects of Water Vapor and Propyl Alcohol Vapors on the Number of Particles of Magnesium Oxide Counted with the Electronic Counter</td>
<td>72</td>
</tr>
<tr>
<td>22.</td>
<td>Optical Density Curve Showing the Charge Distribution on Tobacco Smoke in the Presence of Ammonium Vapor</td>
<td>96</td>
</tr>
<tr>
<td>23.</td>
<td>Optical Density Curve Showing the Charge Distribution on Tobacco Smoke in the Presence of Propylene Glycol Vapor</td>
<td>97</td>
</tr>
<tr>
<td>24.</td>
<td>Optical Density Curve Showing the Charge Distribution on Tobacco Smoke in the Presence of Methyl Alcohol Vapor</td>
<td>98</td>
</tr>
<tr>
<td>25.</td>
<td>Optical Density Curve Showing the Charge Distribution on Tobacco Smoke in the Presence of Water Vapor</td>
<td>99</td>
</tr>
<tr>
<td>26.</td>
<td>Optical Density Curve Showing the Charge Distribution on an Ammonium Chloride Aerosol</td>
<td>100</td>
</tr>
</tbody>
</table>

(Continued)
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>Upper Block: The Effect of Salt Ions in an Atmosphere of 40 Per Cent Relative Humidity on Light Scattered from an Ammonium Chloride Aerosol. Lower Block: The Effect of Water Vapor on Light Scattered by Dry Air in the Absence of Aerosol.</td>
<td>101</td>
</tr>
<tr>
<td>28</td>
<td>The Effects of Organic Vapors on Light Scattered from Ammonium Chloride Aerosols.</td>
<td>102</td>
</tr>
<tr>
<td>29</td>
<td>The Effects of Organic Vapors on Light Scattered from Ammonium Chloride Aerosols.</td>
<td>103</td>
</tr>
<tr>
<td>30</td>
<td>The Effects of an Organic Vapor and Salt Ions on Light Scattered from Ammonium Chloride Aerosols.</td>
<td>104</td>
</tr>
<tr>
<td>31</td>
<td>The Effects of Nitrobenzene on Light Scattered from Ammonium Chloride Aerosols.</td>
<td>105</td>
</tr>
<tr>
<td>32</td>
<td>The Effects of Water Vapor and Organic Vapors on Light Scattered from Propylene Glycol Aerosols.</td>
<td>106</td>
</tr>
<tr>
<td>33</td>
<td>The Effects of Organic Vapors and Salt Ions on Light Scattered from Propylene Glycol Aerosols.</td>
<td>107</td>
</tr>
<tr>
<td>34</td>
<td>The Effects of Organic Vapors and Water Vapor on Light Scattered from Stearic Acid Aerosols.</td>
<td>108</td>
</tr>
<tr>
<td>35</td>
<td>The Effects of Organic Vapors on Light Scattered from Stearic Acid Aerosols.</td>
<td>109</td>
</tr>
<tr>
<td>36</td>
<td>The Effects of Organic Vapors and Salt Ions on Light Scattered from Stearic Acid Aerosols.</td>
<td>110</td>
</tr>
<tr>
<td>37</td>
<td>The Effects of an Organic Vapor and Salt Ions on Light Scattered from β-Naphthol Aerosols.</td>
<td>111</td>
</tr>
<tr>
<td>38</td>
<td>The Effects of Water Vapor and Organic Vapors on Light Scattered from β-Naphthol Aerosols.</td>
<td>112</td>
</tr>
<tr>
<td>39</td>
<td>The Effects of Organic Vapors on Light Scattered from β-Naphthol Aerosols.</td>
<td>113</td>
</tr>
<tr>
<td>40</td>
<td>The Effects of Water Vapor and Some Organic Vapors on Light Scattered from Tin Chloride Aerosols.</td>
<td>114</td>
</tr>
<tr>
<td>41</td>
<td>Effect of β-Radiations on the Aggregation of an Ammonium Chloride Aerosol as Indicated by Light Scattering.</td>
<td>115</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table I.</th>
<th>ELECTRICAL CHARGE DATA FOR VARIOUS AEROSOLS SHORTLY AFTER GENERATION</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>Table II.</td>
<td>ELECTRON CHARGE ON AEROSOL PARTICLES SHORTLY AFTER GENERATION</td>
<td>39</td>
</tr>
<tr>
<td>Table III.</td>
<td>EFFECT OF VAPORS ON LIGHT SCATTERED BY AEROSOLS</td>
<td>61</td>
</tr>
</tbody>
</table>
I. SUMMARY

The present investigation was concerned with the behavior of aerosols and, in particular, with the forces which affect the aggregation of the particles composing the aerosol. The principal objectives were studies of (1) the effect of electrical charge on the aggregation rate, (2) the nature and magnitude of the charges carried by the particles and (3) the nature of other factors influencing aggregation in an aerosol.

Theoretical considerations are discussed which relate to: (1) the loss of aerosol mass by collision with confining surfaces; (2) the loss of number of particles by collision with the container surfaces; (3) the loss of number of particles by aggregation, including the effects of Brownian Motion, van der Waals forces, polydispersity, turbulence and electrical charge; (4) the combined losses from aggregation and from collision with surfaces, and (5) the change in concentration during dilution or build-up of an aerosol. In addition, a recent theory regarding the effect of vapors on aggregation is discussed.

Experimental results are presented which describe the investigations of aerosol generation, electrification and aggregation. Several techniques for aerosol generation are discussed, together with discussions of the aerosol properties which result from the various methods of formation. An aerosol charge analyzer, developed for use in the electrification studies, permitted accurate and rapid determinations of the charge carried by aerosol particles. The degree of electrification and the magnitude of the charges for various aerosols are tabulated, and, whenever possible, comparison is made with the data of other investigators. Methods for altering the aerosol charge characteristics are described; of these methods,
charging by irradiation from a radioactive source was applied to aggregation studies.

Several techniques for evaluating the aggregation of an aerosol are discussed. The sedimentation technique involved measurements of the sedimentation rates of various aerosols. Experiments are described which show the effect of electrification and of certain vapors on sedimentation rates. Another technique utilized measurements of the light scattered by an aerosol before, during and after introduction of a vapor in order to analyze for effects on aggregation. While the sedimentation technique was essentially a static method, the light-scattering technique was applied to a dynamic system, i.e., the aerosol flowed continuously through the analyzer cell. Improvements to light-scattering measurements as well as criticisms of methods used by previous investigators in dealing with vapor effects are discussed. Electron photomicrographs are presented to illustrate the results of both the sedimentation and the light-scattering studies.

Finally, an apparatus was built which permits the aerosol number concentration to be determined electronically. Preliminary investigations with this counter have been devoted mainly to its calibration and evaluation. The results obtained thus far indicate that the instrument will prove suitable for aggregation studies.

The conclusions reached, some of which experience has shown should be applied with caution to systems and conditions other than those employed in this investigation, are that: (1) aerosol particles tend to carry an electrical charge roughly proportional to their surface area; (2) the shape of aggregates composed of several aerosol particles is conditioned by the charge on the particles; (3) the electrification of aero-
sols normally encountered, i.e., as a result of natural ionization, is of relatively minor importance in aggregation; (4) the effect of electrical charge on aggregation has not been satisfactorily distinguished from the effect of charge on the shape of the aggregate; (5) an apparatus for measuring the electrical charge on an aerosol has been developed; (6) certain vapors alter the rate of aggregation of some aerosols; (7) the alteration is more pronounced in the case of liquid aerosols, and (8) electronic counting of aerosol particles is feasible and will be of great value in studying aerosol aggregation.

Continuation of the work is recommended with emphasis being placed on generation processes and the relation between the process and the aerosol's properties. The use of aerosols of more direct interest to the sponsor is also recommended where applicable.
II. INTRODUCTION

A system composed of fine particle matter—either liquid or solid—suspended in gas is called an aerosol. Fogs, mists, dusts and smokes are commonly encountered aerosols, but many others, such as those of organic and plant products, are also quite common yet often go unnoticed. Regardless of their composition, all aerosols have certain similar properties. For example, they scatter light to give beautiful colors, or in dense concentrations they absorb a large fraction of the incident light. There is also a tendency for individual particles to come together in clumps, or aggregates, which results in their falling out of the air at a faster rate than before aggregating.

The general purposes of this project were to study (1) the effects of the electrical charge of an aerosol on the rate of aggregation of the individual particles, (2) the nature of the electrical charge and (3) the nature of other factors affecting the aggregation of an aerosol.
Final Report, Project No. 186-130

III. THEORETICAL CONSIDERATIONS

In this section will be given the mathematical theory relating to the aggregation of aerosols unenleavened by experimental results or comments. Results and analyses of results will follow in other sections.

A. Mass Decrease with Time

It is well known that the rate of change of mass concentration of an aerosol is adequately expressed by the relation

$$\frac{dm}{dt} = -k_1 m$$  \hspace{1cm} (1)

where $m$ is mass concentration of aerosol at time $t$ and $k_1$ is a constant. Integration of equation 1 leads to

$$\ln \frac{m}{m_o} = -k_1 t$$  \hspace{1cm} (2)

where $m_o$ = original mass concentration in suspension at time $t = 0$. Since $m/m_o$ = the fraction of the original weight remaining in suspension, $f_a$, and since the fraction settled, $f_s$, equals $1 - f_a$, equation 2 may be altered to

$$\ln(1 - f_s) = -k_1 t.$$  \hspace{1cm} (3)

In order to show an increase in settling rate by an increase in the slope of a settling curve, equation 3 may be rearranged to the form

$$\ln(\frac{1}{1-f_s}) = k_1 t,$$  \hspace{1cm} (4)

and the data may be plotted as $\frac{1}{1-f_s}$ vs. $t$ on semilogarithmic paper.

B. Number Decrease with Time

1. Surface Losses

The rate of disappearance of particles by collision with wall surfaces has been shown to be proportional to the number of particles in suspension.
Thus,

$$\frac{dn}{dt} = -k_2n$$

(5)

where \(n\) = number of particles in suspension at time \(t\).

When loss of particle number by aggregation is negligible, equation 5 may be integrated to give

$$\ln \frac{n}{n_0} = -k_2t$$

(6)

where \(n_0\) is the original number present at time \(t = 0\). According to equation 6 a plot of particle number versus time on semilogarithmic paper should result in a straight line.

2. Aggregation Losses

a. Brownian Motion. Smoluchowski (1917) studied the coagulation of monodisperse sols in Brownian motion and showed that the probability of a collision between a spherical particle and others in its vicinity is \(4\pi DSn\) where \(n\) is the number of particles per unit volume, \(D\) is the relative diffusion coefficient for any two particles, and \(S\) is the sphere of attraction between each two particles colliding. The total number of such collisions is then \(1/2 (4\pi DSn)^2\). If all collisions are assumed to result in coagulation, then the term \(2\pi DSn^2\) represents the number of particles removed in unit time if \(D\) and \(S\) are the same for each particle. Application of Fick's law of diffusion leads to the expression for the rate of decrease of particle number. Thus,

$$- \frac{dn}{dt} = 2\pi DSn^2$$

(7)

Since all the particles act as centers of attraction for other particles, the diffusion constant for any two colliding particles may be written
\[ D = D_1 + D_2 \]  

where \( D_1 \) and \( D_2 \) are the diffusion coefficients for the individual particles. Furthermore, Smoluchowski points out that the two particles involved in the collision may have different values of \( S \), and, in accordance with the kinetic theory of gases, the actual value of \( S \) is

\[ S = \frac{1}{2} (S_1 + S_2) \]  

where \( S_1 \) and \( S_2 \) are the radii of the spheres of attraction for the individual particles. If it is assumed that \( S_1 = kr_1 \) and \( S_2 = kr_2 \), then

\[ S = \frac{k}{2} (r_1 + r_2) \]  

where \( r \) is the radius of the particle.

If the value of \( k \) is 2, then the particles will unite only upon collision; if \( k \) is greater than 2, the particles will be drawn into collision upon passing within a certain distance from each other. Equation 7 may be rewritten as

\[ -\frac{dn}{dt} = k\eta (D_1 + D_2)(r_1 + r_2)n \]  

Einstein (1905), assuming a number of particles distributed randomly in a fluid, found that the diffusion coefficient of the particles could be expressed as

\[ D = \frac{RT}{N} B \]  

where \( N \) is Avogadro's number, \( R \) and \( T \) are the gas constant and temperature and \( B \) is the mobility. For \( B \), Smoluchowski used the value obtained by Stokes, \( \frac{1}{6\pi\eta r} \), where \( \eta \) is the viscosity of the medium and \( r \) the radius of the spherical particles. In the case of smokes having particle radii less
than 0.1 micron, it is necessary to use the Stokes mobility as modified by Cunningham (1910),
\[ B = \frac{1 + A \frac{\Delta}{r}}{6 \mu \eta r} \]  
(13)

where \( A \) is a constant and \( \lambda \) is the mean free path of the gas molecules. When the value of the mobility is substituted into equation 8,
\[ D = \frac{RT}{6 \eta \eta N} \left( \frac{1 + A \frac{\Delta}{r_1}}{r_1} + \frac{1 + A \frac{\Delta}{r_2}}{r_2} \right) . \]  
(14)

If the diffusion coefficient given by equation 14 is inserted into equation 11, the result is
\[ -\frac{dn}{dt} = k N \frac{RT}{6 \eta \eta N} \left( \frac{1 + A \frac{\Delta}{r_1}}{r_1} + \frac{1 + A \frac{\Delta}{r_2}}{r_2} \right) (r_1 + r_2) n^2 . \]  
(15)

For a homogeneous smoke \( r_1 = r_2 = r \), and, hence,
\[ -\frac{dn}{dt} = \frac{2 RT k}{3 \eta N} \left( 1 + A \frac{\Delta}{r} \right) n^2 . \]  
(16)

If the effective radius for coagulation is equal to the geometric radius of the particle, \( k \) is equal to 2, and equation 16 reduces to
\[ -\frac{dn}{dt} = \frac{4 RT k}{3 \eta N} \left( 1 + A \frac{\Delta}{r} \right) n^2 . \]  
(17)

Since the rate of decrease of particle number is given as \( Kn^2 \), it is obvious that the coagulation constant for a homogeneous smoke is
\[ K = \frac{4 RT k}{3 \eta N} \left( 1 + A \frac{\Delta}{r} \right) . \]  
(18)

b. Polydispersity. The values of the coagulation constant deduced from experimental observations always exceed the values predicted
from equation 18 by 20 to 30 per cent, and the disagreement has usually
been ascribed to the polydisperse nature of the smoke being examined.
Consequently, Patterson, Whytlaw-Gray and Cawood (1929) introduced an
empirical factor of 1.25 in equation 18 to reconcile the departure of
observed from theoretical values.

Tikhomirov, Tunitskii and Petryanov (1942) have studied in more de-
tail the effects of polydispersity and van der Waals forces of attrac-
tion on the coagulation constant. The results of these studies indicate
that the difference between the theoretical and the observed coagula-
tion constants is largely due to the forces of attraction between par-
ticles rather than to the polydisperse nature of the aerosols examined.
The distribution function of the particles with respect to their radii at
time t is defined as \( f(r,t) \). Then the decrease of particle number per cu-
bic centimeter per second is given by

\[
- \frac{dn}{dt} = \frac{1}{2} \int_{0}^{\infty} \int_{0}^{\infty} K(r,x) f(r) f(x) \, dr \, dx \tag{19}
\]

where \( K(r,x) \) is the coagulation constant, \( x = L/r \), \( r \) is the radius of
the particles, and \( L \) is the distance between the centers of the parti-
cles. Application of the theoretical coagulation constant in equation
19 leads to

\[
- \frac{dn}{dt} = \frac{hR^2}{3 \eta N} \left[ 1 + \bar{r} \left( \frac{\bar{r}}{r} \right) + \bar{A} \Lambda \left( \frac{\bar{r}}{r} \right) + \bar{A} A \bar{A} \Lambda \bar{A} \Lambda \left( \frac{\bar{r}}{r^2} \right) \right] n^2 \tag{20}
\]

where \( \bar{r} = 1/n \int f(r) \, r \, dr \) is the mean value of \( r \), and \((\bar{r}/r)\) and \((\bar{r}/r^2)\) are
the mean values of \( 1/r \) and \( 1/r^2 \). Equation 20 shows that a detailed
knowledge of the particle size distribution is not necessary to describe
the coagulation process, but that a knowledge of the mean values of \( r \), \( 1/r \)
and \( 1/r^2 \) is sufficient. The increase of the coagulation rate due to poly-
dispersity is expressed through a factor of polydispersity, \( f \), as

\[
f = \frac{K_{\text{poly}}}{K_{\text{mono}}} = \frac{1 + \frac{1}{r} \left( 1 + \frac{1}{r^2} \right) + A^\lambda \left( 1 + \frac{1}{r^2} \right) + A^\lambda \frac{1}{r}}{2 \left( 1 + A^\lambda \frac{1}{r} \right)}.
\]  (21)

The experiments of Tikhomirov, et al., show that the increase in coagulation caused by polydispersity amounts to only a few per cent, certainly not to 25 per cent as had been postulated. Since, however, experimental values of \( K \) often exceed theoretical values by as much as 25-30 per cent, it is evident that considerations other than polydispersity must influence the coagulation constant.

c. Van der Waals Forces. Tikhomirov and coworkers therefore studied the van der Waals forces of interaction between the particles. The increase of the rate of coagulation of a monodisperse system caused by van der Waals forces was found to be independent of particle size but dependent on the distance between the centers of the particles. Hence, the coagulation constants were modified by a factor \( \gamma \), which depends on the nature of the substance but not on particle size. Thus,

\[
K_{\text{mono}} = \gamma \frac{LRT}{3 \eta N} \left( 1 + A^\lambda \frac{1}{r} \right),
\]  (22)

and

\[
K_{\text{poly}} = \gamma \frac{LRT}{3 \eta N} \left( 1 + \frac{1}{r} \left( 1 + \frac{1}{r^2} \right) + A^\lambda \left( 1 + \frac{1}{r^2} \right) + A^\lambda \frac{1}{r} \right).
\]  (23)

These equations may be used for experimental determination of the factor \( \gamma \), or \( \gamma \) may be calculated by means of the constant of van der Waals forces. With aerosols of mineral oil, tricresyl phosphate and sulfuric acid, \( \gamma \) varied from 1.22 to 1.30. Hence, the forces of attraction between the particles account for the fact that the experimental values of \( K \) exceed theo-
retical value by 25-30 per cent. The decrease of particle number with time due to coagulation may then be determined by

\[- \frac{dn}{dt} = Kn^2\]  \hspace{1cm} (24)

where \(K\) is given by equations 22 or 23.

d. Electric Charge. The derivations thus far have ignored the possible effect of electric charges on the aerosol particles. Only a few investigators have studied the relation between electrification and rate of concentration change. Whytlaw-Gray and Patterson (1932) found no difference between the rate of coagulation of ammonium chloride smokes which had been charged with X-rays and those which were uncharged. Gillespie (1952) points out that the experiments of Whytlaw-Gray and Patterson were limited to smokes having considerably smaller particles than are sometimes encountered and, consequently, having a smaller electric charge per particle since the charges carried by particles are roughly proportional to the surface area of the particles.

Kunkel (1948) presented a theoretical analysis of the average growth of a charged particle in a cloud caused by electrostatic attraction. Application of his equation requires a knowledge of particle size and charge distribution. With the assumption of a highly simplified distribution, it was found that the rate of growth of a particle was negligible if

\[\left|qq_o\right| \frac{N}{r^2} < 10^{-10}\]  \hspace{1cm} (25)

where \(q\) is the charge on a particle in electrons, \(q_o\) is the average charge of the particles of one sign in electrons, \(r\) is the average radius of the
particles in microns, and \( N \) is the number of particles per cubic centimeter.

If the value \( 10^{10} \) is exceeded, aggregation would result in a decrease in \( N \), an increase in \( r \) and perhaps a decrease in \( |qq_0| \) until equation 25 was satisfied. The time for this change is assumed to be a few seconds.

Gillespie (1952) studied more highly charged aerosols. To examine the effect of electric charges on aggregation, he separated the coagulation constants into classifications according to the type of collision. Thus, for a symmetrical charge distribution,

\[
K = K_0 f_0^2 + 2 K_{0q} f_q f_0 + \frac{f_0^2}{2} (K_{+-} + K_{--}), \tag{26}
\]

where \( K_0, K_{0q}, K_{+-} \) and \( K_{--} \) denote constants descriptive of the aggregation between neutral particles, neutral and charged particles, particles with opposite charges and particles with like charges, respectively. The fraction of the particles which are neutral is symbolized by \( f_0 \), the fraction charged by \( f_q \). For unsymmetrical charge distribution, \( f_q \) may be determined by the equation

\[
f_q^2 = 4 f_+ f_- \tag{27}
\]

For collisions due to Brownian motion between neutral and charged particles, the coagulation constant is given by the Smoluchowski theory as

\[
K_{0q} = \frac{4}{3} \frac{RT}{\eta N}. \tag{28}
\]

Since Gillespie dealt with particles having an average radius of nearly one micron, neglecting the Cunningham correction factor \( (1 + \frac{2}{r}) \) in equation 28 was justified. For aggregation between particles of opposite sign,

\[
K_{+-} = \frac{\frac{2}{3\eta} \frac{2}{q} \left( \frac{\overline{r}}{r} \right)}{1 - e^{-\frac{Nq^2G^2}{2\pi RT} \left( \frac{\overline{r}}{r} \right)}}. \tag{29}
\]
For particles of the same sign,

\[
K_{\pm} = \frac{2}{3\eta} \frac{q^2}{\overline{I}/r} \, e^{-\frac{Nq^2}{2RT} \left( \frac{I}{r} \right)^2}.
\]  

(30)

In equations 29 and 30, \( \overline{q} \) represents the average charge of one sign and \( \overline{I}/r \) the average value of the reciprocal radius. For unsymmetrical distributions of charges, \( \overline{q}^2 = ( \text{average negative} ) \times ( \text{average positive} ) \).

e. Turbulence and Gravity Settling. Gillespie also analyzed the effects of turbulence and gravity settling on the coagulation constants in a manner similar to the Brownian motion effects study given above and found that these effects could be described by the following relations: for turbulence,

\[
(K_{+-})_T = \frac{4}{3} \left[ 8w^3 + \frac{2q^2}{\pi\eta} \left( \frac{I}{r} \right) \right],
\]

(31)

\[
(K_{-+})_T = \frac{4}{3} \left[ 8w^3 - \frac{2q^2}{\pi\eta} \left( \frac{I}{r} \right) \right],
\]

(32)

and

\[
(K_{0q})_T = \frac{32w^3}{3},
\]

(33)

and for gravity settling,

\[
(K_{+-})_S = 2\pi V_0 \overline{r}^2 + \frac{2}{3\eta} \overline{q}^2 \left( \frac{I}{r} \right)
\]

(34)

and

\[
(K_{-+})_S = 2\pi V_0 \overline{r}^2 - \frac{2}{3\eta} \overline{q}^2 \left( \frac{I}{r} \right)
\]

(35)

where \( V_0 \) is the relative sedimentation velocity between two particles and \( w \) is the velocity gradient in the vicinity of particles in a turbulent medium.
Neglecting the aggregation between particles of like sign, Gillespie arrived at the equation

\[ K = \gamma K_o + A \,fq^2 \,\bar{q}^2 \left( \frac{1}{\bar{r}} \right) . \]  

(36)

In equation 36, \( \gamma K_o \) is given by

\[ \gamma K_o = \gamma \left( \frac{1}{3} \frac{RT}{\eta N} + 2 \pi \nu_o \, \bar{r}^2 + \frac{32}{3} \, \bar{r}^3 \right) . \]  

(37)

The constant \( A \) in equation 36 is approximated by

\[ A = \gamma \left\{ \frac{1}{3 \eta} \left( 1 + 4 \pi \nu_0 \right) + \frac{1}{e^{-\frac{Nq^2}{2RT}} \left( \frac{1}{\bar{r}} \right) - 1} \right\} . \]  

(38)

If the movement of the particles is limited to the effects of Brownian motion, equations 37 and 38, respectively, reduce to

\[ \gamma K_o = \gamma \frac{1}{3} \frac{RT}{\eta} \]  

(39)

and

\[ A = \gamma \left( \frac{1}{3 \eta} \cdot \frac{1}{e^{-\frac{Nq^2}{2RT}} \left( \frac{1}{\bar{r}} \right) - 1} \right) . \]  

(40)

Since many aerosol studies deal with polydisperse systems having particles in the Cunningham size range, it is necessary to modify equation 39 in the manner of equation 23; then, substitution into equation 36 yields

\[ K = \gamma \frac{2}{3} \frac{RT}{\eta N} \left[ 1 + \bar{r} \left( \frac{1}{\bar{r}} \right) + A \lambda \left( \frac{1}{\bar{r}} \right) + A \lambda \bar{r} \left( \frac{1}{\bar{r}^2} \right) \right] + \]  

\[ \gamma \left[ \frac{1}{3 \bar{r}} \cdot \frac{1}{e^{-\frac{Nq^2}{2RT}} \left( \frac{1}{\bar{r}} \right) - 1} \right] f_q^2 \, \bar{q}^2 \left( \frac{1}{\bar{r}} \right) . \]  

(41)
When the aerosol in question is uncharged, $f_q$ is 0, and equation 41 reduces to equation 23. On the other hand, consider a highly charged aerosol, say, 90 per cent charged. For simplicity, a monodisperse system, radius one micron, is assumed. Then at a temperature of 20°C, the first term of equation 41 reduces to the value obtained by Smoluchowski; that is,

$$\gamma \frac{2}{3} \frac{RT}{N^2} \left[ 1 + \bar{F} \left( \frac{1}{x} \right) \right] = 1.75 \times 10^{-8} \text{ cm}^3/\text{min.}$$

According to Gillespie, the second term of equation 41 is given approximately by

$$\gamma \left[ \frac{1}{3\eta} \cdot \frac{1}{e} \frac{-Nq^2 (\frac{1}{x})}{2RT} - 1 \right] f_q^2 q^{-2} \left( \frac{1}{x} \right) = 1 \times 10^{-13} \cdot f_q^2 q^{-2} \left( \frac{1}{x} \right)$$

where $\bar{q}$ is in electron units and $r$ in centimeters. For $\gamma = 1.25, f_q = 0.9$ and $r = 1$ micron, the second term is $1 \times 10^{-9} \bar{q}^2$. It is seen that a charge of only a few electron units increases the coagulation constant several fold over the value predicted by the Smoluchowski theory. Thus, it seems that the importance attributed to electrification by Gillespie is in conflict with previous theories.

3. Combined Surface and Aggregation Losses

Treatment of aerosols having a high concentration of particles per unit volume must take into account decrease in particle number due to both coagulation and surface losses. That is,

$$- \frac{dn}{dt} = Kn^2 + k_2n.$$  \hspace{1cm} (42)

Integration of equation 42 leads to
The coagulation constant, $K$, for a certain aerosol may be evaluated by the methods described in the previous section. The constant $k_2$ may be determined by experiment using dilute aerosols, i.e., aerosols having concentrations such that particle number loss by coagulation is negligible.

### 4. Dilution

It is often of interest to know the change of concentration of a smoke within a chamber as the smoke is continuously withdrawn from the chamber. The concentration change may be expressed by

$$-dn = \frac{d}{V} n \, dt$$

where $d$ is the rate of dilution, $V$ is the volume of the chamber, $n$ is the particle concentration in the chamber and $t$ is time. For a constant rate of dilution,

$$\ln \frac{n}{n_0} = -\frac{d}{V} t$$

or

$$n = n_0 e^{-\frac{d}{V} t}$$

where $n_0$ is the initial concentration. Data of this sort are conveniently plotted on semilogarithmic paper to obtain linear extrapolations.

The equations governing the process of filling a chamber with an aerosol are similar to those developed for the dilution of an aerosol. Thus,

$$dn = n_0 \frac{d}{V} dt - n \frac{d}{V} dt$$
and

\[ n = n_0 \left(1 - e^{-\frac{d}{V} t}\right) \]  

where \( n \) is the concentration of particles in the chamber at any time \( t \).

C. Effect of Vapors

Because of the apparently conflicting results of many investigators studying the effect of vapors on the aggregation of aerosols and because of the difficulty encountered in the interpretation of the results, few theories have been offered to explain the behavior of aerosol particles in a vapor-laden atmosphere. The recent investigations of Fedoseev, Manakin and Domentianova (1952) serve to clarify the mechanism involved. These authors suggested that substances which lower the vapor pressure of water, for example, can significantly increase the rate of sedimentation of water droplets, since collision between droplets of the water is not prevented by a cushion of water vapor. Surface tension was found to be irrelevant by these same investigators.
IV. EXPERIMENTAL INVESTIGATIONS

A. Aerosol Generation

The aerosols used in this study were generated by various means. The method most extensively used involved the generator described by LaMer (1949). The essential components of this generating unit are: (1) the aerosol generator proper; (2) air pressure and flow regulators; (3) an air-drying train consisting of columns of silica gel, calcium chloride, and anhydrous phosphoric acid; (4) air flow meters and control valves; and (5) heaters and controls.

This generator, originally constructed in accordance with the specifications given by its originators, has been altered in several ways. Alterations to the unit included the addition of insulation and the installation of thermocouples. The gooseneck tube connecting the boiler and re-boiler flasks was equipped with a separate heating element. Control of air flow rates in the apparatus was obtained through the use of a standard air pressure regulator operating in series with a flow regulator (a Cartesian manostat manufactured by the Emil Greiner Company of New York).

The LaMer generator has been found suitable for the production of aerosols from readily vaporizable materials. With careful control of temperatures and flow rates, a nearly monodisperse aerosol may be obtained. Aerosols of stearic acid, ammonium chloride, glycerol, propylene glycol, dioctyl phthalate, naphthalene, β-naphthol and tin chloride have been successfully prepared with the device.

Elutriation techniques have been described by DallaValle (1948). When an elutriation technique was used for aerosol generation, a stream of air was passed upward through a column 15 cm. in diameter and 80 cm. high.
The substance to be elutriated was placed on the bottom of the column in
the path of the incoming air stream and was agitated to prevent channel-
ing and clogging of ports. Particles whose terminal settling velocities
were less than the linear velocity of the air stream were carried out of
the elutriation chamber and thus constituted the solid phase of the aero-
sol. The elutriation technique is generally limited to solid substances,
but it could be used in the case of low-vapor-pressure liquid droplets.
Dry powders were dispersed with the apparatus in this study.

Magnesium oxide smokes were formed by burning ribbons of magnesium
metal in the air. Combustion methods of aerosol formation are simple and
rapid, but the smokes thus produced exhibit wide variations in particle
size and in complexity of the aggregates.

Both solid- and liquid-phase aerosols were generated with atomizers.
The solid-phase aerosols were formed by dissolving the solid or mixing a
powder in a volatile solvent before atomization; after the spray issued
from the nozzle, the solvent evaporated, leaving a nucleus of the solid
substance. The mists were generated by atomizing a nonvolatile liquid,
the droplets of which persisted for several hours. Three types of nozzles
have been used: DeVilbiss Nebulizers Nos. 140 and 180 and a "Chicago"
atomizer.

Aerosols were also generated by directing a blast of air at a sample
of dust; these aerosols were used in a few cases for comparative purposes.

B. Aerosol Electrification

1. Evaluation

a. Apparatus. The charge on individual dust particles or liquid
droplets of microscopic size dispersed in the air influences their behavior
and affords a means for studying other phenomena. Studies were undertaken to determine the effect of electric charge on the aggregation of aerosol particles. The first step in the study was the development of an apparatus by which the state of the aerosol's electrification could be measured. As is usually the case, a variety of instruments have been used by previous investigators, and some of these warrant a brief description.

The apparatus of Wells and Gerke (1919) subjected air-borne particles to an alternating electrical field, thereby causing charged particles to oscillate and to move in zigzag paths when the aerosol was passed through the field. The results were recorded photographically. White and Hill (1948) used the Wells and Gerke method to obtain the charge on each particle from the amplitude of its vibration but could not distinguish between positively and negatively charged particles.

In this type of apparatus used by Kunkel (1950) and Kunkel and Hansen (1950), successive positions of individual particles settling under the influence of gravity through a horizontal electrical field were recorded photographically. The charge on each particle was then determined from the path taken by the particle. Aside from being a tedious and time-consuming analysis for statistically precise results, the technique had one serious limitation. Small convection currents resulting from temperature differences between opposite walls or ends of the settling chamber could easily invalidate the results.

Gillespie (1952) used an instrument in which a thin stream of the aerosol was drawn within a sleeve of clean air between two parallel vertical electrodes maintained at a high potential difference. The charged particles were deposited on microscopic slides placed on the inner sur-
faces of the electrodes, while the neutral particles passed through the apparatus and were collected in a thermal precipitator. The electric charge distribution was then obtained from a microscopic analysis of the deposits.

The apparatus developed independently in this work also employed a stream of aerosol particles moving at a relatively slow velocity but moving at a velocity compared to which convection currents were insignificant. The behavior of a great number of particles was analyzed so that statistically acceptable results were obtained in a short time. While the apparatus to be described here was, therefore, not subject to the limitations of the previous apparatus, it had limitations which will be discussed later. Several designs and modifications, one of which recorded the data photographically, were constructed. Since the latest apparatus represents the best design yet, only this one will be discussed in detail.

The complete apparatus is shown pictorially in Figure 1; the main component is given in detail in Figure 2. Since several components of the electrical system were also used in the counting studies, the circuit diagram is given in the section describing the particle counter. The aerosol to be examined entered the aerosol chamber through a special nozzle at the bottom center, flowed vertically upward and exhausted from the top center. Flow through the chamber may be either upward or downward. An upward flow has been found to be more satisfactory with very small particles while a downward flow is better with the larger particle sizes. When a downward flow is used, the electrodes are rotated 180° about the axis of their supporting arms from the position shown in Figure 2. The
Figure 1. Aerosol Charge Analyzer.
Figure 2. Diagram of Aerosol Charge Analyzer.
Final Report, Project No. 186-130

nozzle is shown separately in Figure 3. As examination of Figures 2 and 3
will reveal, the significant feature of the nozzle through which the
aerosol entered the chamber was a slit oriented so that the narrowest di-
mension of the resulting stream—approximately 0.5 mm.—was presented to
an observation port. Electrodes were located so that the electrical field,
when established, was at right angles to the plane of observation. A col-
limated beam of light entered the chamber horizontally through a port lo-
ated at angles of 45° and 135°, respectively, with the plane of the elec-
trodes and the plane of observation. A light trap was provided 180° from
the port through which the light entered. The interior of the chamber was
blackened to eliminate light reflections. A twice-magnified image of a
small horizontal section of the aerosol stream was formed by the lens sys-
tem in the observation port at the plane of a movable, vertical slit. The
slit was 0.1 mm. wide. An image of the slit was in turn formed on the
sensitive element of a 1P21 photomultiplier tube, and the output of the
photomultiplier tube was registered on a meter. Therefore, moving the
photomultiplier tube across the plane of observation and noting the meter
readings constituted one determination.

An aerosol stream having a rectangular cross section was used so that
from the position of observation, the stream would appear to originate from
a narrow zone and yet would contain sufficient particles to produce a
bright image when dispersed by the electrical field. A stream of clean air
flowing at about the same rate surrounded the aerosol stream. This sheath
of air prevented the spread of the aerosol stream when there was no elec-
trical field by preventing contact between the aerosol stream and the stag-
nant body of air in the chamber. When the electrical field was energized,
Figure 3. Aerosol Inlet Tube.
the surrounding sheath of air acted as a zone into which charged particles might move without undergoing a change in vertical velocity. The electrodes were shaped and located as shown in Figure 2 to avoid interference with the light field and were polished to eliminate sharp points and edges.

The major pieces of auxiliary equipment were a high voltage source, a pump and a power supply for the photomultiplier tube. The high voltage supply used in this work was capable of generating a potential difference between the electrodes up to 20,000 volts and was constructed so that, when one electrode was positive, the other was negative by the same amount. Its circuit diagram is given in Figure 4. Gradients between the electrodes of about 4,000 volts/cm. were generally employed. The pump which moved the aerosol through the apparatus was obtained from George A. Thiberg, Cedar Knolls, N. J., and was originally designed for the aeration of small fish ponds. It was altered to provide a suction port. An ordinary microscope lamp provided the illumination. A patent application on the charge-analyzing apparatus is being processed.

b. Procedure. Obtaining the proper flow rates of the smoke and air-sheath streams to give laminar conditions of the desired magnitude through the analyzing chamber sometimes required careful adjustment. Hence, it was found advantageous to employ a pump having an adjustable pumping rate and also to provide a by-pass valve. As used in this investigation, the pump provided a slight suction and was therefore attached so as to exhaust the analyzing chamber. Additional valves were provided on the line between the smoke reservoir and the analyzing chamber and on the air sheath inlet. It was found expedient to remove the photomultiplier tube
Figure 4. Circuit Diagram of High Voltage Supply.

- **C$_1$**: 500 MMF, 20 K.V.
- **C$_2$**: 500 MMF, 20 K.V.
- **C$_3$**: 500 MMF, 20 K.V.
- **C$_4$**: 500 MMF, 20 K.V.

- **R$_1$**: Meter Multiplier Consists of 9 Res. in Series to Total 100 Megohms
- **T$_1$**: 15000 V Neon Transformer With C.T Grounded To Case Internally
- **T$_2$**: Filament Trans With Pri. to Sec. Insulated For 20 K.V.
(including the housing and the slit) while adjusting the flow so that the
effect of each adjustment could be observed visually.

After a sharply defined smoke stream had been obtained and while the
stream was being viewed, the voltage on the electrodes was increased un-
til the desired spreading of the aerosol resulted. The spreading chosen
was that which did not cause appreciable corona discharge and which gave
maximum separation of the smoke without causing the stream to disperse
to such an extent that large parts of it became faint. A spreading of the
original aerosol stream to ten times its original width was regarded as
the minimum necessary to give adequate resolution. When the instrument
was thus adjusted for measurements, the photomultiplier tube was put in
place.

Making the measurement merely required moving the photomultiplier
tube across the image of the aerosol stream with the electrical field
energized and recording the photomultiplier tube output as a function of
position.

c. Results. The upper block of Figure 5 shows the appearance
of a stream of tobacco smoke passing through the apparatus without ener-
gizing the electrical field. When the aerosol stream looked like the one
shown in the lower block of Figure 5, a traverse with the photomultiplier
tube resulted in a curve such as that shown in Figure 6. Scanning the
negative, from which the print of Figure 6 was made, with a photodensitom-
eter gave a similar curve. This was the method of analysis in earlier
models. Generally, curves having a single mode resulted; the signifi-
cance of the multimodal curve is discussed later. Classification of the
particles on the basis of electrical charge into three rather distinct
Figure 5. Behavior of a Tobacco Smoke Passing Through No Electrical Field (Upper Block) and Passing Through a Gradient of 5,000 volts/cm. (Lower Block).
Figure 6. Distribution of the Charges on Tobacco Smoke Particles.
groups is evident. One group of particles did not deviate from its course, while the other groups moved to the right and to the left of center, leaving, in this particular case, a zone of largely free space between themselves and the neutral central zone. Figures 22 through 25 in the Appendix present electrification data on tobacco smoke aerosols in the presence of various vapors. There appears to be no significant difference in the electrification of tobacco smoke because of the presence of the foreign vapors investigated. Figure 26 shows a typical optical density curve for an ammonium chloride aerosol formed by atomizing an alcoholic solution of the salt. Results of examinations of several aerosols are given in Table I. The high degree of electrification exhibited by the atomized ammonium chloride aerosol (80 per cent charged) demonstrates the influence of this method of aerosol generation on electrification, for an ammonium chloride aerosol formed by low-temperature volatilization in the LaMer generator showed only slight electrification (5 per cent charged). The principles underlying the differences in the electrification of aerosols due to the method of formation will be discussed later.

Complete analysis of the charge associated with the aerosol particles entails consideration of several factors. The amount of lateral deflection of a particle in the electrical field is a function of the mass of the particle, the charge, the field strength and the flow rate of the aerosol stream through the electrification chamber. An analysis of the electrical field between cylindrical electrodes has been summarized by Earnwell (1938). If the boundary conditions imposed by the design of the apparatus and by the experimental technique are applied, an expression may be derived which relates the deflection of the particle passing through
## TABLE I

### ELECTRICAL CHARGE DATA FOR VARIOUS AEROSOLS SHORTLY AFTER GENERATION

<table>
<thead>
<tr>
<th>Aerosol</th>
<th>Method of Formation</th>
<th>Approximate Average Dia. (microns)</th>
<th>Fraction Positive</th>
<th>Fraction Negative</th>
<th>Fraction Charged</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tobacco</td>
<td>Burning</td>
<td>0.1 - 0.25</td>
<td>40</td>
<td>34</td>
<td>74</td>
</tr>
<tr>
<td>Tobacco in Ammonia Vapor</td>
<td>Burning</td>
<td>0.1 - 0.25</td>
<td>41</td>
<td>41</td>
<td>82</td>
</tr>
<tr>
<td>Tobacco in Propylene Glycol Vapor</td>
<td>Burning</td>
<td>0.1 - 0.25</td>
<td>41</td>
<td>40</td>
<td>81</td>
</tr>
<tr>
<td>Tobacco in Methanol Vapor</td>
<td>Burning</td>
<td>0.1 - 0.25</td>
<td>39</td>
<td>42</td>
<td>81</td>
</tr>
<tr>
<td>Tobacco in Water Vapor</td>
<td>Burning</td>
<td>0.1 - 0.25</td>
<td>43</td>
<td>39</td>
<td>82</td>
</tr>
<tr>
<td>Clay</td>
<td>Elutriation</td>
<td>3 - 5</td>
<td>47</td>
<td>44</td>
<td>91</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>LaMer Generator</td>
<td>0.2</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>Low-Temperature Volatilization</td>
<td>---</td>
<td>3*</td>
<td>4*</td>
<td>7*</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>LaMer Generator</td>
<td>0.2</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>Low-Temperature Volatilization</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>5*</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>Dispersed from Alcohol Solution by Atomizer</td>
<td>0.8 - 1.0</td>
<td>39</td>
<td>43</td>
<td>82</td>
</tr>
<tr>
<td>Sugar</td>
<td>Dispersed from Alcohol Solution by Atomizer</td>
<td>0.8 - 1.0</td>
<td>40</td>
<td>39</td>
<td>79</td>
</tr>
</tbody>
</table>

*These data were taken from Whytlaw-Gray and Patterson (1932) and Patterson, Whytlaw-Gray and Cawood (1929).*
the field to the charge of the particle. The accompanying sketch will be useful in the following analysis. The electrical forces on a particle in the field surrounding cylindrical electrodes arranged parallel to one another, as in this investigation, have also been discussed by Harnwell. Electrodes of infinite length were assumed, however. The following derivation assumes that the finite length of the electrodes will not greatly affect the analysis and that the velocity of the particle will not be materially altered by the acceleration and deceleration effects of the electrical field.

The force causing horizontal deflection of the particle is given by

\[ F_x = \frac{q_L}{2\pi K_0} \cdot \frac{q}{d} \cos \theta \]  

where \( q_L = \) charge per unit length of electrode,
\[ q = \] charge of the particle,
If \( \cos \theta \) is replaced by its equivalent \( c/2 \), equation (29) becomes

\[
F_x = \frac{q_L c q}{2 \pi K_0 d^2} \cdot
\]  

But from geometric considerations, \( d^2 = y_1^2 + (c/2)^2 \), so

\[
F_x = \frac{q_L c q}{2 \pi K_0} \cdot \frac{1}{y_1^2 + (c/2)^2} \cdot
\]  

Included in the discussion by Harnwell are the relations

\[
q_L = C_L V ,
\]  

and

\[
C_L = \frac{\pi K_0}{\cosh^{-1} (c/2b)}
\]

where \( C_L \) = capacity per unit length and

\( V = \) potential difference.

Combination of equations (52) and (53) yields

\[
q_L \frac{\pi K_0}{\cosh^{-1} (c/2b)} = \frac{V}{\cosh^{-1} (c/2b)} .
\]

Substitution of equation (54) into equation (51) gives

\[
F = \frac{V c q}{2 \cosh^{-1} (c/2b)} \cdot \frac{1}{y_1^2 + (c/2)^2} \cdot
\]  

Equation (55) may be simplified by setting \( \cosh^{-1} (c/2b) \) equal to \( w \) where

\[
w = \ln \left[ \frac{c}{2b} + \frac{1}{2} \sqrt{(c/b)^2 - 4} \right].
\]

Hence, equation (55) becomes

\[
-34-\]

\[
\]
Final Report, Project No. 186-130

\[ F_x = \frac{Vc_q}{2w} \cdot \frac{1}{y_1^2 + (c/2)^2} \cdot \]  

(56)

Assuming now that the viscous resistance \((6\pi \eta r \frac{dx}{dt})\) force is much greater than the inertial resistance \((ma)\) force and then equating the viscous resistance to \(F_x\),

\[ 6\pi \eta r \frac{dx}{dt} = \frac{Vc_q}{2w} \cdot \frac{1}{y_1^2 + (c/2)^2} \]  

(57)

where \(\eta\) = viscosity of the medium,

\(r\) = radius of the particle and

\(\frac{dx}{dt}\) = velocity of the particle in a horizontal direction.

Rearrangement of equation 57 leads to

\[ \frac{dx}{dt} = \frac{Vc_q}{12\pi \eta rw} \cdot \frac{1}{y_1^2 + (c/2)^2} \]  

(58)

The term \(y_1\) is a function of time. Since the velocity of the particle in the vertical direction is \(V_o\), it is evident that

\[ y_1 = V_o t - y_o \]  

(59)

Substituting the equivalent of \(y_1\) from equation 59 into equation 58 gives

\[ \frac{dx}{dt} = \frac{Vc_q}{12\pi \eta rw} \cdot \frac{1}{(V_o t - y_o)^2 + (c/2)^2} \]  

(60)

Integration yields

\[ x = \frac{Vc_q}{12\pi \eta rw} \int_{t=0}^{t=t} \frac{dt}{(V_o t - y_o)^2 + (c/2)^2} \]  

(61)

By suitable transformation, equation 61 can be reduced to

\[ x = \frac{Vc_q}{6\pi \eta rw} \left[ \tan^{-1}(2y_1/c) + \tan^{-1}(2y_0/c) \right] \]  

(62)

The geometry of the electrification chamber used in the present study
is such that the distance from the tip of the aerosol inlet tube to the electrode axis \(y_o\) is approximately equal to the distance from the electrode axis to the point of observation \(y_1\). Hence,

\[
x = \frac{Vq}{3\eta r w v_o} \tan^{-1}(2y_1/c).
\]

Application of the appropriate conversion factors yields

\[
x = \frac{1.6 \times 10^{-12} Vq}{3\eta r w v_o} \tan^{-1}(2y_1/c)
\]

where \(x\) = horizontal deflection of particle, cm.,
- \(V\) = potential difference, volts,
- \(q\) = charge on particle, electrons,
- \(\eta\) = viscosity of medium, poises,
- \(r\) = radius of particle, cm.,
- \(v_o\) = vertical velocity of particle, cm./sec.,
- \(y_1\) = vertical distance from electrodes to point of observation, cm.,
- \(c\) = separation between centers of electrodes, cm.,
- \(b\) = radius of electrode, cm., and
- \(w = \ln \left[ (c/2b) + (1/2) \sqrt{(c/b)^2 - 4} \right].\)

The foregoing solution was simplified by the assumption that the inertial resistance was negligible in comparison to the viscous resistance. If the inertial resistance term is considered, equation 58 becomes

\[
\frac{d^2x}{dt^2} + \frac{6\eta r}{m} \cdot \frac{dx}{dt} = \frac{Vq}{2mw} \cdot \frac{1}{\left( v_o t - y_o \right)^2 + (c/2)^2}
\]

where \(m\) = mass of the particle. For simplification, let

\[
K_1 = \frac{6\eta r}{m},
\]
and

\[ K_2 = \frac{V_0 Q}{2\pi m (c/2)^2}; \]

then

\[ \frac{d^2 x}{dt^2} + K_1 \frac{dx}{dt} = K_2 \left[ \frac{1}{1 + \left( \frac{V_0 t - y_0}{c/2} \right)^2} \right]. \]  

(66)

The term of equation 66 in brackets is of the form \( \frac{1}{1+u^2} \) where \( u = \frac{V_0 t - y_0}{c/2} \).

Since \( \frac{1}{1+u^2} \) is the derivative of \( \tan^{-1} u \), a solution of the form

\[ x = A \tan^{-1} \left( \frac{V_0 t - y_0}{c/2} \right) + B \]

(67)

is suggested wherein \( A \) and \( B \) are constants. Application of the boundary conditions \( x = 0 \) when \( t = 0 \) yields

\[ x = A \left[ \tan^{-1} \left( \frac{V_0 t - y_0}{c/2} \right) - \tan^{-1} \left( \frac{-y_0}{c/2} \right) \right].\]  

(68)

Substitution of the values of \( dx/dt \) and \( d^2 x/dt^2 \), determined from equation 68, into equation 66 leads to

\[ A \left[ K_1 + \frac{(-2) \left( \frac{V_0 t - y_0}{c/2} \right) \left( \frac{V_0}{c/2} \right)}{1 + \left( \frac{V_0 t - y_0}{c/2} \right)^2} \right] = \frac{K_2 (c/2)}{V_0}. \]  

(69)

The constant \( A \) cannot be equated to a term involving the variable \( t \).

Consideration of numerical values in consistent (cgs) units, however, shows that \( K_1 \) is of the order of \( 10^6 \) where the term \( \frac{(-2) \left( \frac{V_0 t - y_0}{c/2} \right) \left( \frac{V_0}{c/2} \right)}{1 + \left( \frac{V_0 t - y_0}{c/2} \right)^2} \) is less than one. Hence, the term of equation 69 in brackets is approximately equal to \( K_1 \), and

\[ A = \frac{K_2}{K_1} \cdot \frac{(c/2)}{V_0}. \]  

(70)
When the constant $A$ of equation 68 is replaced by its approximate value given by equation 70, equation 68 reduces to equation 63; therefore, the assumption of negligible inertial resistance is justified. Equation 64 was used to calculate the charge carried by aerosol particles, using information obtained from the charge distribution curves.

The minimum deflection—determined from the width of the relatively clear space between the central stream and the charged particle area of Figure 5 showing tobacco smoke dispersed in the electrical field—corresponded to singly charged particles with a maximum diameter of 0.6 micron. This result is in agreement with the data of several investigators who found that the charge carried by particles is roughly proportional to surface area and that very small particles seldom carry multiple charges. According to equation 64, photometric analysis of an electrified aerosol perfectly homogeneous with respect to particle size would give charge distribution curves exhibiting a series of maxima and minima in the charged particle zone, each peak corresponding to a different multiple charge on the particle. Therefore, the departure from this predicted peak curve to the relatively smooth curve of Figure 6 indicates nonhomogeneity of particle size. Calculations by equation 64 may be based on a median particle size, thus permitting estimations of the fractions of particles carrying multiple charges, but the accuracy of the estimation is dependent on the deviation of the distribution of particle sizes from the median value. For the tobacco smoke aerosols used in the present study, it was found that the deflection from the central stream to the peak of the curve in the charged particle area corresponded to singly charged particles from 0.1 micron to 0.25 micron in diameter. This result, in excel-
lent agreement with the observations of Gibbs (1924) and many recent observations on the size of tobacco smoke particles, is evidence that the relatively clear zone between neutral and charged particle areas arises because most of the charged particles carry a single electron charge.

Equation 64 has been used to calculate the average charge carried by particles in several different aerosols. The results are summarized in Table II.

**TABLE II**

**ELECTRON CHARGE ON AEROSOL PARTICLES SHORTLY AFTER GENERATION**

<table>
<thead>
<tr>
<th>Aerosol</th>
<th>Method of Formation</th>
<th>Average Particle Diameter (microns)</th>
<th>Average Charge per Particle (electrons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tobacco Smoke Burning</td>
<td>0.1 - 0.25</td>
<td>1 - 2</td>
<td></td>
</tr>
<tr>
<td>Magnesium Oxide Burning</td>
<td>0.8 - 1.5</td>
<td>8 - 12</td>
<td></td>
</tr>
<tr>
<td>Clay Elutriation</td>
<td>2 - 4</td>
<td>20 - 40</td>
<td></td>
</tr>
<tr>
<td>Stearic Acid LaMer Generator</td>
<td>0.2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ammonium Chloride LaMer Generator</td>
<td>0.2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ammonium Chloride At Atomization of an Alcoholic Solution</td>
<td>0.8 - 1.5</td>
<td>12 - 15</td>
<td></td>
</tr>
</tbody>
</table>

It is interesting to note that the average charge of a clay particle is essentially the same value reported by Kunkel (1950) for a quartz dust of corresponding particle size. The results showing that single electron charges are carried by the charged particles in aerosols formed with the LaMer generator serve as confirmation of the work of White and Hill (1948), who found that only about two per cent of the charged particles of an aerosol produced with a LaMer generator carried double charges.
2. Alteration
   
a. Apparatus

   (1) Corona Discharge. In order to assess the effect of an aerosol's electrification on its behavior, altering the charge distribution of the aerosol was deemed necessary so that measurements could be made for both the original and the altered aerosol. Accordingly, an electrostatic charging device similar to that described by LaMer (1952) was constructed, but the results obtained with this type of charging were discouraging. Another device, also based upon the corona discharge technique, was fashioned so that one electrode was shaped in the form of a disc while the other tapered to a point. The aerosol particles passing through the field between the disc and the tapered tip became charged, but most of the particles thus charged were deposited on the surface of the disc, leaving an aerosol too dilute for accurate measurement.

   (2) Friction. Gillespie (1952) found that the electrification of a silica aerosol, formed by directing a blast of air on the powder, was dependent upon the air pressure used. Kunkel (1950), on the other hand, found the electrification of a similar aerosol to be quite independent of the air pressure. Experiments on clay aerosols conducted in this investigation supported the results of Kunkel; no appreciable change in the charge distribution of a clay aerosol was detected, although the air pressure varied from 10 to 40 pounds per square inch, and the glass tube through which the clay was blown varied from 3 to 10 feet in length.

   (3) Radioactivity. Irradiation has been found to be a most satisfactory method for the charging of aerosol particles. In the
present investigation, the aerosol to be charged was passed through a tube containing either polonium or radium. The aerosol particles passing through the ionized zone about the radioactive source picked up both positively and negatively ionized air molecules and became charged. The polonium was obtained as the ionizing element used in static elimination devices, and the radium source was obtained from the United States Radium Corporation.

b. Effect of Vapors. Aerosols of ammonium chloride, magnesium oxide and tobacco smoke were examined with the charge analyzer, both before and after being aged in atmospheres saturated with water vapor and with propylene glycol vapor. The purpose of these experiments was to determine whether the action of certain vapors in affecting the aggregation of aerosols was exerted through a change in the charge distribution of the aerosol.

c. Results. Little change in the charge distribution of a magnesium oxide aerosol (charged by thermal emission in the process of generation) was evident after the aerosol had aged in the presence of polonium. This result may be explained on the basis of the random charging by the air ions resulting from the alpha radiation, i.e., a particle, whether charged or not and whether charged positively or negatively, is about as likely to pick up a positive as a negative ion. On the other hand, approximately half the particles of an ammonium chloride aerosol generated with a LaMer generator, and hence essentially uncharged, became charged after being subjected for a short time to the alpha radiation of the polonium. Subsequent experiments showed that ammonium chlo-
ride aerosols could be charged by passage near either the polonium or radium sources and that, in contrast to corona discharge methods, deposition on the tube walls about the radioactive source was insignificant. However, only one or two electron charges were picked up by the charged particles so that, although an appreciable fraction of the particles became charged, the magnitude of the charge was small. No significant change in the electrification of aerosols of ammonium chloride, magnesium oxide and tobacco smoke due to the presence of water or propylene glycol vapors was detected.

C. Aerosol Aggregation

1. Sedimentation Technique

a. Apparatus. Two sedimentation chambers were used to determine the rates at which aerosol particles settled out of suspension. The first was a cylindrical glass tube with brass top and bottom sections. A removable sliding section in the bottom plate of the chamber was constructed with circular slots into which glass plates were fitted. In making a sedimentation analysis, the glass plates were exposed periodically, and the quantity of particles which settled during the time interval of the exposure was determined by methods described in more detail in the following sections. The sedimentation chamber was fashioned from a glass tube having an inside diameter of 15 centimeters and a height of 80 centimeters. The glass collection plates were 7.5 centimeters in diameter.

The second sedimentation chamber was a cubical box constructed from transparent plastic. The length of a side was 20 inches, giving it a total surface area of approximately 17 square feet, as compared with less than 5 square feet for the cylindrical chamber. A circular door 12 inches
in diameter was cut in one of the sides of the plastic box to permit easy access to the inside. Sedimented samples were again collected on slides 7.5 cm. in diameter.

b. Procedure. The procedure for introducing an aerosol into either sedimentation chamber varied with the aerosol being examined. Ammonium chloride aerosols were formed with a LaMer generator and blown directly into the sedimentation chamber through a port in the base. When the chamber had been filled with the aerosol, collector slides were put in place at the bottom of the chamber, and samples were taken after periods of 5, 15, 30, 60, 90, and 150 minutes and again after twenty four hours. The time involved in changing plates between samples was only a few seconds and was disregarded.

Magnesium oxide aerosols were formed by burning a specified amount of magnesium ribbon in a flask and transferring the contents of the flask to the sedimentation chamber. Approximately two minutes were required to burn the ribbon and transfer the smoke to the sedimentation chamber, after which samples were collected as described above.

When the effects of electrical charge were being investigated, the aerosol was passed over the radioactive source before being introduced into the chamber.

The effect of vapors on the sedimentation rate of aerosols was determined by introducing the vapor and the aerosol into a sedimentation chamber and measuring the amount of aerosol settled with time by chemical methods to be described below. In the case of an ammonium chloride smoke formed continuously with the LaMer generator, the main aerosol stream was mixed with a diluent air stream which was introduced either directly or
after passage through a gas-washing bottle containing the liquid whose vapor was to be investigated. Thus, by controlling the flow rates of the various streams, it was possible to subject an aerosol to atmospheres varying from one nearly void of any vapor to one nearly saturated. Because the formation of magnesium oxide aerosols by burning was an intermittent process, the vapors to be investigated in this case were formed in a different manner. The magnesium oxide smoke resulting from the burning of a specified amount of ribbon was collected in a large flask and blown with dry air into the sedimentation chamber where the atmosphere had been previously conditioned with the desired vapor. Generation of this vapor was accomplished by vaporizing a quantity of liquid, calculated to bring the atmosphere of the chamber to the desired relative saturation, in a small heating tube located in the sedimentation chamber.

Because electron photomicrographs of aerosol particles in various stages of aggregation showed the greatest effect with propylene glycol and water vapor, these two substances were emphasized in the sedimentation studies.

c. Methods of Analysis. Sedimentation experiments have been conducted with aerosols of magnesium oxide and ammonium chloride. Since the samples taken in the analyses were very small in quantity, chemical methods were employed to obtain quantitative results. In addition, electron photomicrographs were taken of samples of the settled particles.

When magnesium oxide was being investigated, the magnesium content of a sample was determined by the versenate technique which consists essentially of the following analytical steps: first, dissolving in hydrochloric acid the sample which has been collected; next, adjusting the
pH of the solution to 10 with ammonium hydroxide; and finally, titrating with versenate (solution of the disodium salt of tetraacetic acid), using Eriochromesblack T as the indicator.

The amount of ammonium chloride settled in an increment of time was determined through measurements of the chloride content by Fajan's method as given by Kolthoff and Stenger (1947). This latter technique consists of dissolving the sample in distilled water and titrating with a silver nitrate solution, using dichlorofluorescein as the indicator. A silver nitrate solution approximately one-hundredth normal has been found suitable as the titrating reagent. With the versenate technique, the end point is evidenced by the change of the solution from a pink to a blue color, while with Fajan's method, the end point is evidenced by the sudden change of the solution from colorless to red or rose.

d. Results. The sedimentation of ammonium chloride aerosols, uncharged and charged by radioactive means to the degree described in a preceding section, was measured, and results are presented in Figure 7. The method of presenting sedimentation data in Figure 7 follows the scheme suggested by equation 4. It is evident that the fraction of ammonium chloride aerosol settled at any particular time was not measurably changed by charging the particles. It is interesting to note that, although the sedimentation rates of the uncharged and the charged ammonium chloride aerosols were equal, the shape of the charged particle aggregates differed markedly from the shape of the uncharged aggregates. Typical electron photomicrographs are presented in Figure 8. From a number of such photomicrographs it was possible to compare the number of particles joined in an aggregate for the cases of the charged and uncharged aerosols. These results are presented in Figure 9.
Figure 7. The Sedimentation of Charged and Uncharged Ammonium Chloride Particles.
Figure 8. Photographs of Aggregated Ammonium Chloride Particles.
Figure 9. Comparison of the Number of Particles Comprising an Aggregate for Uncharged and Charged Ammonium Chloride Aerosols.
The effect of vapors on the sedimentation of ammonium chloride and magnesium oxide aerosols is shown in Figures 10 and 11. It appears that in both cases the sedimentation rate is increased by the presence of water vapor and reduced by the presence of propylene glycol vapors. To clarify the relationship between sedimentation rate and aggregation, electron microscope slides were placed in the bottom of the sedimentation chamber, and samples of the aerosols were taken at various periods of time. The results for magnesium oxide are shown in Figure 12 and for ammonium chloride in Figure 13. As shown in Figure 12, the aggregates of magnesium oxide particles in a humid atmosphere appear to be more compact and dense than the dry aggregates, and hence would be expected to settle faster. Aggregates in an atmosphere of propylene glycol also appear to be more compact than the dry aggregates and, on that basis alone, would be expected to settle faster than the dry aggregates. Reference to Figure 11 shows that this did not result. Closer examination of Figure 12 shows that there were more small, discrete aggregates in the case of the propylene glycol atmosphere. Since, from Stokes' law, the terminal settling velocity is proportional to the square of the diameter, it follows that, on the basis of size, the magnesium oxide aggregates in the presence of propylene glycol vapors would settle at a slower rate. Measurements with the aerosol charge analyzer have shown that the presence of water vapor or propylene glycol vapor has no effect on the charge distribution of either a magnesium oxide or an ammonium chloride aerosol.

2. Dynamic Technique

   a. Apparatus. While difficulties are encountered in generating an aerosol having the same characteristics, e.g., particle size distribution,
Figure 10. The Sedimentation of an Ammonium Chloride Aerosol in Various Atmospheres.
Figure 11. The Sedimentation of a Magnesium Oxide Aerosol in Various Atmospheres.
Figure 12. Magnesium Oxide Particles Obtained by Sedimentation from Various Atmospheres and After Various Intervals of Time.
Figure 13. Ammonium Chloride Particles Obtained by Sedimentation from an Atmosphere of 50 Per Cent Relative Humidity After Various Intervals of Time.
concentration, etc., from one experiment to the next, it is relatively easy to generate an aerosol for a period of a few minutes having constant characteristics. Therefore, a system was devised which utilized a stream of aerosol and which indicated a result in a matter of minutes. Results were indicated by the light scattered from the aerosol, and the analysis of the data depended on an interpretation of the scattering measurements and on electron photomicrographs of precipitated samples. This system was used primarily for the purpose of estimating the effect of foreign vapors on an aerosol's behavior, but some experiments were also planned so as to be indicative of the effect of electrical charge. The system proved to be quite sensitive.

Aerosols formed with the LAMER generator were used in the dynamic method. The necessary components of the entire system are shown in Figure 14. These included, in addition to the LAMER generator, a Tyndall meter with a light-scattering chamber, an aerosol-mixing chamber, wet- and dry-bulb thermometers, a chamber where foreign vapors might be introduced into the air stream, and a thermal precipitator.

The Tyndall meter and auxiliary light-scattering chamber used on a previous Chemical Corps project (Contract No. W-18-035-CW3-1313) were modified to permit direct mounting of the chamber on a spectrometer tripod. The photoelectric cell was mounted in the normal position of the telescopic eyepiece, and a microscope projection lamp served as a light source. Fluctuations of voltage to both the light source and the phototube circuits of the Tyndall meter were minimized through the use of a voltage stabilizer manufactured by the Kelly-Koett Manufacturing Company, Inc., Covington, Ky. A spherical five-liter flask provided a suitable aerosol reservoir and chamber where mixing between the aerosol and foreign
Figure 14. Schematic Diagram of Aerosol Apparatus.
vapors could take place. Contact of foreign vapors with the air stream was generally accomplished by bubbling the air through a porous plate immersed in the liquid whose vapors were to be investigated. The thermal precipitator, described in another report by Dalla Valle, et al. (1951), was modified by the addition of a special aerosol inlet so that samples could be taken without having the precipitator inside the aerosol chamber. This modification consisted of lengthening parts No. 960-5 and No. 960-6, Chemical Corps Drawing No. D-93-1-960, so that a port could be drilled into the precipitation cavity.

b. Procedure. The procedure will be explained with the aid of Figure 14. The aerosol stream at the point of leaving the condensing column of the LaMer generator was diluted immediately with a stream of dry air and was then diluted a second time just prior to entering the aerosol-mixing chamber. This design permitted the introduction of either pure air or vapor-laden air at the second dilution point, while the first dilution ensured an aerosol sufficiently dispersed to be quite stable. Vapors in the desired concentration could be introduced into the main aerosol stream of constant particle concentration by adjusting the flow rates in the various diluent streams. A wet- and dry-bulb thermometer in the exit stream indicated the relative saturation at all times. All tubes were made as short as possible. In general, the only agitation in the mixing chamber was produced by the turbulence of the incoming and outgoing aerosol streams. The stream leaving the mixing chamber was passed through another small chamber where a light beam was partially scattered by the aerosol particles. The scattering (at an angle of 140° with the incident light beam) was detected by the phototube and indicated by the Tyndall meter.
A change in the light scattered by the aerosol because of the presence of the vapor was clearly apparent about six minutes after introducing the vapor. Calculations showed that this time interval was sufficient for the vapor-laden atmosphere to replace most of the former contents of the mixing chamber. In air devoid of aerosol the contribution of vapor to scattering was undetectable; therefore, the change in scattered light was believed to be related to aggregation. This will be discussed in a later section.

Since only a short period of time was required to obtain the indication, the limitation of time-consuming measurements was avoided; that is, the probability of a change in the aerosol from causes other than those resulting from the introduction of vapor was small.

Determinations of the effect of the change in question were made by recording the scattered light intensity before, during and after the change. Electron photomicrographs were taken of the aerosol particles from a dry atmosphere (relative humidity less than five per cent) and from a vapor-laden atmosphere. The thermal precipitator was used to obtain samples of the aerosols for the electron microscope studies.

c. Results. Figures 15 and 16 are typical curves showing the effects of various vapors on the light scattered from an aerosol; other curves are given in Figures 27 through 41 in the Appendix. As may be seen, vapors of water, propylene glycol, glycerol, methanol, ethanol, phenol, carbon tetrachloride, oleic acid, acetic acid, 5 per cent NaCl solution, 30 per cent FeCl₃ solution and nitrobenzene were tested on aerosols of ammonium chloride, propylene glycol, stearic acid, β-naphthol and tin chloride. In most cases, the relative saturation of the vapor in the system was kept at forty per cent, though the actual concentration of the foreign vapors in the aerosol
Figure 15. The Effects of Water Vapor on Light Scattered from Ammonium Chloride Aerosols.
Figure 16. The Effects of Organic Vapors on Light Scattered from Ammonium Chloride Aerosols.
differed widely because of the differences in vapor pressure (higher vapor pressures meaning greater concentration). The relative effect of the vapors is summarized in Table III.

Other experiments were devised to improve the chance for contacts between vapor molecules and aerosol particles. To investigate the effect of turbulence on the aggregation of aerosols in the presence of vapors, a small fan was placed inside the aerosol-mixing chamber and tests were run as before. The increased turbulence from the fan action had a negligible effect on the light-scattering characteristics of the ammonium chloride, stearic acid and β-naphthol smokes, but was sufficient to condense nearly all of the propylene glycol mist on the chamber surfaces.

The light-scattering characteristics of an ammonium chloride aerosol were altered by the presence of a radioactive substance in the mixing chamber. Ordinarily the presence of water vapor was accompanied by an increase in the intensity of the scattered light. When radium was placed in the dry aerosol stream, the introduction of water vapor did not cause as significant an optical effect as when the emitter was not present. When the radium was removed, an increase in scattered light intensity occurred.

The result of changing the method of water vapor generation was also investigated. The humidity produced by bubbling air through water, possibly accompanied by the electrification of water droplets through rupture of the liquid surface, resulted in greater light scattering than humidity produced by passing air over boiling water, though the same relative humidity was maintained in both cases. Bubbling the diluent air through cold water resulted in greater light-scattering than bubbling the air through hot water. Since the same water vapor concentration was maintained in the two tests, the difference may possibly be attributed to the
TABLE III
EFFECT OF VAPORS* ON LIGHT SCATTERED BY AEROSOLS

<table>
<thead>
<tr>
<th>Vapor Effectiveness of Aerosols of</th>
<th>Ammonium Chloride</th>
<th>Magnesium Carbonate</th>
<th>Propylene Glycol</th>
<th>Stearic Acid</th>
<th>β-Naphthol</th>
<th>Tin Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>++++</td>
<td>0</td>
<td>+</td>
<td>0</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>Propylene Glycol</td>
<td>++++</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Glycerol (heated)</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl Alcohol</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ethyl Alcohol</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>Phenol</td>
<td>+</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>++</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl solution, 5%</td>
<td>++++</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeCl₃ solution, 30%</td>
<td>++++</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The symbol ++++ indicates a very pronounced effect, a single + indicates a slight effect, and other plus signs indicate intermediate effects. The symbol 0 indicates no effect.
decreased surface tension at elevated temperatures and the consequent decreased violence accompanying surface rupture. To substantiate this effect, an experiment was conducted in which air was bubbled through water, the surface tension of which had been decreased by adding a small amount of a surface-active agent. The scattered light was diminished after the addition of the surfactant.

3. Counting Technique

a. Apparatus. The need for an accurate method of determining aerosol concentration has often been expressed in connection with quantitative evaluation of electrification, concentration and foreign vapor effects on aerosol aggregation. Preliminary studies indicated that a light-scattering technique might be used to obtain the desired information, and accordingly a particle counter has been constructed. A picture of the counter chamber is given in Figure 17. Some changes have been made on this unit since this picture was taken, but the changes do not significantly alter its operation. With some exceptions, the design of the apparatus is the same as that presented by Gucker and O'Konski (1949). The explanation of its operation is accompanied by Figure 17. A carbon-arc light is focused to give an image of the electrode crater at a slit in the end of the light tube. This slit is not visible in the figure. Lenses within the light tube collect the light and focus an image of the slit at the center of the particle counter. The aerosol stream is pulled through the aerosol inlet tube (1/16-inch inside diameter) and through the counter by means of a small pump. At the center of the counter, the aerosol stream intercepts the light beam. Light scattered by the particles at right angles to the axis of incident light is collected by lenses within the counter.
Figure 17. Aerosol-Counting Chamber.
tube and focused on the sensitive element of a 1P21 photomultiplier tube. This tube actuates the counter. If the aerosol being examined is sufficiently dilute, individual particles will produce individual pulses in the photomultiplier tube and counter circuits, and the number concentration of the aerosol may be determined by dividing the particles counted per unit time by the flow rate of aerosol through the counter. The dimensions of the aerosol inlet tube, the dimensions of the light beam and the aerosol velocity must be carefully regulated if pulse interference is to be avoided. The recovery time interval of the photomultiplier tube is high enough that the tube response is an accurate measure of the pulses for rather rapid counting. The complete circuit diagram of the scaler unit and preamplifier for the photomultiplier tube is given in Figure 18.

Below a certain particle size, the pulse signal caused by the scattered light from the particle will be indistinguishable from the random noise signals. Thus, the instrument will count accurately only those particles generating a pulse of amplitude greater than the noise level. Gucker and O'Konski (1949) reported a critical size of about one micron. However, the lenses of the present apparatus are different from the lenses in the apparatus of these investigators; the 1P21 photomultiplier tube used here is considerably more sensitive than the 931A photomultiplier tube of Gucker and O'Konski and a more intense light source is being used. Hence, a smaller critical particle size is expected, but its value has not been definitely established.

All surfaces within the counter chamber were covered with black velvet cloth, and a filtered air sheath surrounding the aerosol stream effectively prevented diffusion of the particles within the counter chamber.
Figure 18. Circuit Diagram of Scaler Unit and Preamplifier.
Preliminary tests with the apparatus were made with a Model 1070 Multiscaler, manufactured by the Atomic Instrument Company, Cambridge, Massachusetts. The instrument was borrowed from another laboratory of the Engineering Experiment Station. Several major changes to the multiscaler were necessary for improved operation however. Therefore, a decimal scaler unit was built to conform to all the requirements.

b. Procedure. As yet, most of the counting experiments have been designed to furnish an evaluation of the counting system. Such an evaluation is not easy to make, but several lines of approach have been investigated with varying degrees of success.

Obtaining liquid-dispersed and uniform-sized samples of solid particles for aerosol formation by spraying was first attempted. The method of Hauser and Lynn (1940), requiring the use of a supercentrifuge, was followed. This approach was used because it was hoped that both the particle size and the concentration of the resulting aerosol could be obtained. In practice, this was not borne out because liquid atomizers tend to concentrate the solids and, also, because closely sized solid fractions were not obtained from the centrifuging operation. Finely divided clays were employed as the solid component.

Relatively uniformly sized fractions of solids were also prepared by air elutriation. These were not as monodisperse as the materials prepared in the liquid phase, however.

A bacterial culture (Serratia marcescens) of known bacteria count was used in the preparation of other aerosols. Atomizing was, of course, employed. The bacteria proved to be of little value for calibration purposes because the nutrient, as well as cellular debris, formed particles of a wide range of sizes.
To calibrate and evaluate the counter, microscopic examination of thermally precipitated samples was employed. For the desired result with this procedure, the counter was operated for an interval of several minutes while an aerosol stream was drawn through the instrument at a known rate; the thermal precipitator was operated for a similar interval of time with the same rate of aerosol flow. The instrument-counted number and the number obtained microscopically were then compared. It was found that best results were obtained when the counting instrument was operated near its maximum resolution as indicated by an oscilloscope.

Further evidence of the operation of the counter was obtained by counting an aerosol as it was being diluted and analyzing the results in accordance with equation 46.

The procedures used in counting studies of aggregation may be explained by reference to Figure 19. Aerosol from a reservoir was pulled through the inlet at the top of the chamber and out the exit port at the base. The stream was observed visually, and when a flow of the desired magnitude and concentration was obtained, the photomultiplier tube was placed in its position as shown in Figure 19, and counts were recorded at various time intervals. If the aerosol was generated in a continuous manner (e.g., the LaMer generator method), samples were pulled through the counting chamber from a vented reservoir which was continuously being replenished with aerosol. If the aerosol was generated in a discontinuous manner (magnesium oxide burning, dry dispersal of clay, etc.), sampling from a reservoir gradually reduced the concentration of the aerosol. In some experiments it was desirable to maintain an essentially constant aerosol concentration while withdrawing samples for counting studies. To meet this requirement, a rubber balloon (the type used in weather studies)
Figure 19. Aerosol-Counting Apparatus and Auxiliary Equipment.
was used as an aerosol reservoir, and the pump of the counting apparatus was adjusted to withdraw a slightly higher aerosol flow than would have resulted from the positive pressure inside the balloon. This type of reservoir contracted in size as aerosol was removed, thus keeping a constant particle concentration except for aggregation and surface loss effects. The aggregation and surface losses were evaluated by noting the gradual concentration decrease with time as aerosol samples were continuously withdrawn from the balloon. The effect of vapors on aggregation and surface losses was determined by vaporizing an amount of liquid into the balloon during the course of counting measurements.

c. Results. Gucker and O'Konski (1949) based the evaluation of their particle counter largely on the shape of the pip appearing on an oscilloscope screen. On this basis, the counter built in this work is quite satisfactory and an improvement over the counter of Gucker, et al. However, this was not deemed to be sufficient proof of the counter's accuracy. To the present time, other attempts at calibration have shown the counter to be relatively independent of particle concentration and to give actual counts of the correct order of magnitude for particles above about one-quarter of a micron in radius. Failure to agree more closely or to include smaller particles is believed to be due as much to the sampling and microscopic technique used in the calibration as to the counting instrument.

Specifically, counting an aerosol made by spraying a dilute solution of *Serratia marcescens* gave a somewhat smaller count than the number known to be in the solution but gave a larger count than obtained for the aerosol by cultural methods. On the other hand, with an aerosol
made by dispersing a dry clay sample, a discrepancy of $10^2$ particles/cc. was found, the microscopic count indicating the greater number of particles. Since particles considerably below the limits of resolution of the counter were counted with the microscope, this result is not surprising. With a LaMer-generated dioctyl phthalate aerosol, agreement within a factor of 10 was found, the microscopic count being higher. Again, particles below counter resolution may have been counted with the microscope. The counting consistency of the apparatus over wide ranges of particle concentration was obtained from an experiment in which a clay aerosol was formed in a large reservoir. The aerosol was constantly diluted by a stream of air passing through the reservoir, and a sample of the contents was continuously withdrawn through the particle counter. As reference to equation 46 shows, the decrease in the number of particles in the reservoir with time should be expressed by a linear relation on semilogarithmic grid if perfect mixing in the reservoir is assumed. The experimental results, given in Figure 20, show that consistent counts were obtained over a wide range of particle concentrations.

Figure 21 shows the rate of concentration decrease of a magnesium oxide aerosol contained in the balloon reservoir. The upper line shows the surface and aggregation losses in a dry atmosphere. The middle line shows the change resulting from the introduction of water vapor, and the lower line shows the effect of propyl alcohol vapor. Since the particle concentrations in the balloon were in all cases less than $10^5$ per cc., aggregation losses were small, and the data were plotted on a semilogarithmic grid in accordance with equation 6. It should be noted that there was a significant change immediately after the vapor introduction but an insignificant change in the slope of the curves later.
Figure 20. Decrease of Particle Number with Dilution.
Figure 21. Effects of Water Vapor and Propyl Alcohol Vapors on the Number of Particles of Magnesium Oxide Counted with the Electronic Counter.
Considerable difficulty was encountered in the counting of *Serratia marcescens*, and no data whatsoever have been obtained on the activities of this bacteria in the air. Aerosols containing the bacteria were formed by atomization with DeVilbiss Nebulizers Nos. 40 and 180, but samples of the settled aerosol particles indicated that a significant fraction of the particles was material other than bacteria, e.g., cellular debris. Accordingly, attempts, as yet incomplete, have been made to establish conditions (fresh cultures, dilute cultures) so that all counts recorded in the analysis of such an aerosol will be due to the bacteria.
V. DISCUSSION OF RESULTS

A. Aerosol Generation

1. Electrical Charge

As shown in Table I, the method of formation greatly influences the electrical character of an aerosol. The high-temperature reactions taking place in the burning of magnesium ribbon and tobacco, because of thermal electron emission, give rise to electrified smokes with approximately equal numbers of positive and negative charges and with a large range of charges carried by the particles. Whytlaw-Gray and Patterson (1932) confirm the experimental result of approximately equal amounts of these particles carrying charges of opposite sign and report that some highly charged smokes appear to have a slight excess of positively charged particles. This result is in complete accord with the present findings. The excess of positive particles is considered to be due to the more ready removal of negative ions because of their greater mobility. This confirmation of results is encouraging, for present results were obtained in a matter of minutes. Previous investigators had resorted to a procedure of examining many particles individually.

Mists formed by passage of a liquid through an atomizing nozzle are also electrified. This is due to the violent breaking-up of the liquid into droplets, according to Gilbert and Shaw (1925). All aerosols formed with a nebulizer were found to be rather highly electrified, a result which demonstrates the influence of the manner of generation on the ultimate electrification of the aerosol.

Ammonium chloride smoke produced by low-temperature volatilization in the LaMer generator exhibited only slight initial electrification, but
when a smoke of the same material was formed with the nebulizer, only a small percentage of the particles was not charged.

One would expect aerosols formed by elutriation to be electrified. Frictional effects during the elutriation process give rise to charges on the particles, and consequently an aerosol produced by this means will be electrified. It is well to note that the action of friction has been attributed to the presence of adsorbed gases. Further discussion of the relation between friction effects and charge is given in a later section.

2. Dispersity

All aerosols other than those produced by controlled low-temperature volatilization (LaMer generator method) were quite polydisperse. Careful regulation of temperatures and flow rates in the LaMer apparatus made it possible to obtain aerosol particles essentially uniform in size. The average particle size of the aerosols produced by this method varied from 0.2 to 0.7 micron, depending upon the adjustment of the controls. The particle concentration of aerosols formed with the LaMer generator was also influenced by the air flow rates and operating temperature. The conditions employed were such that the aerosol concentrations seldom exceeded $10^6$ per cc.

The magnesium oxide smokes exhibited a wide range of particle sizes. Electron photomicrographs showed that the individual particles were cubic and were grouped into aggregates of varying complexity, usually exhibiting chain-like structures.

The atomization method for aerosol formation gave polydisperse systems when liquids containing solids or when solutions were used. If solids of one size had been obtained, atomizing a slurry made from them
would obviously have given a monodisperse aerosol. Neither sedimentation nor centrifugation were continued until quantities of accurately sized particles were obtained, however, because of the extended periods of time which would have been required.

Elutriation also gave aerosols exhibiting a wide size range although it is theoretically possible, by means of repeated elutriation at different flow rates, to obtain a sample having a specific size. Examination of clay and magnesium carbonate aerosols formed by elutriation showed that the solid component existed in aggregates rather than as discrete particles.

3. Relation of Charge and Frictional Effects

Studies of the electrification of a clay aerosol, produced by blowing the clay through a glass tube with a high-velocity jet of air, indicated that resulting electrification was relatively independent of the violence of the dispersal. This result is in complete agreement with the observations of Kunkel (1950). The studies of Gillespie (1952), however, indicate that increased air pressure in the blast caused increased charges on the particles. Both Gillespie and Kunkel used quartz dusts. Kunkel noted that the number of impacts between particles presumably varied according to the amount of turbulence during dispersion, and considered two mechanisms as explanations for the charging process. The most likely is that charge production occurred at the first separation of the contiguous particles and the charges only possibly redistributed themselves slightly at subsequent collisions, which would not affect their magnitude appreciably. Another possible mechanism was based upon the assumption that the charge distribution reached some kind of an equilibrium after comparatively little friction, so that any further impacts
and additional friction would not change the resulting charge noticeably. Subsequent experiments showed that the evidence was overwhelmingly in favor of a charge distribution on separation of contacting surfaces. Therefore, if a blast of air was sufficient to cause most of the separations between clay particles in a sample, it is likely that an increase of air pressure would not greatly alter the magnitude or distribution of the charges. On the other hand, if less than this pressure existed, charging might be expected to vary with the pressure.

B. Aerosol Electrification

1. Evaluation

The procedure for obtaining electrification data with the aerosol charge analyzer has been described in a preceding section. Three possible limitations of the apparatus construction and experimental procedure warrant discussion, however. At relatively low velocities the charging of particles by passage through ducts appears to be a direct function of the velocity of the particles [DallaValle (1948)], and since this velocity was kept at an extremely low value, it would seem unlikely that an aerosol could become charged in this manner. This assumption was justified by the examination of an aerosol known to be uncharged at the time of generation and found to be uncharged after passage through the slit and electrical field.

The second problem involves the possible effect of hindered light scattering, where there is a possibility that the total light scattered by the aerosol stream might be less than the sum of the light scattered by the individual particles. According to Sinclair (1950), particles scatter light essentially independently of one another when the distance
between the particles is 10 or preferably 100 times the radius of the particles. In aerosols having a particle radius of one micron and a number concentration of $10^6$ per cc., the volume associated with each particle is $10^{-6}$ cc., the distance of particle separation is approximately the cube root of $10^{-6}$ cc. or $10^{-2}$ cm., and thus the ratio of separation to radius is $10^{-2}/10^{-4}$ or 100. For a 10-micron particle aerosol of the same number concentration, the ratio is reduced to 10. In such an aerosol some interference between the scattering by neighboring particles would be expected, but such high concentrations are seldom found in practice. With the exception of an elutriated clay aerosol with a median diameter of three to five microns, the aerosols used in this study exhibited median diameters less than one micron. Since the concentration of the clay aerosol was of the order of $10^5$ per cc. and concentrations of the other aerosols never exceeded $10^6$ per cc., the assumption of independent light scattering is justified.

When photographs of the aerosol stream in an electrical field were taken and the resulting negative analyzed, there is a question concerning the photography. It has been shown that, in order to ensure an accurate analysis from film negatives, exposure conditions (light intensity and time) must be chosen so that the optical density of the negative is a linear function of the incident light. Proper choice of exposure was determined by calibration of the film according to the procedure recommended in a publication of the Eastman Kodak Company (1950). The characteristic curve used in establishing the relationship between the exposure and the optical density of the negative was based on an exposure scale which was variable in intensity rather than time, since time variation leads to errors caused by failure of the reciprocity law.
The method of varying the intensity was based on the inverse square relationship between the distance of the light source and the illumination of the exposure plane. Calibration was made by taking photographs with the camera located at various distances from a pinpoint light source and relating the optical density of the negatives thus obtained to the corresponding exposure. Particular care was exercised to operate in the linear range of the calibration and to avoid any overexposure of the negatives showing aerosol streams dispersed in the electrical field. The outer fringes of a dispersed aerosol stream do not contain sufficient particles to expose a negative adequately; hence these regions appear underexposed. The use of the nonlinear (underexposed) part of the calibration curve was of minor significance, however, since the outer fringe of the dispersed aerosol represents less than two per cent of the total aerosol.

While the photographic technique for electrification measurements gave values to within about 10 per cent of the true values, there are certain difficulties inherently associated with photographic methods. For example, the exposure conditions are different for each aerosol and must be chosen with meticulous care. Calibration curves must be established for each new film strip. These and some lesser limitations suggested replacement of the camera with a photomultiplier tube, whereby curves similar to those obtained by photometric analysis of film negatives could be obtained directly by a single traverse of the photomultiplier tube across the area of the dispersed aerosol particles.

2. Alteration

a. Natural. The relation between an aerosol's electrification and its method of generation have been discussed. In accordance
with the observations of other investigators, the results of the present study showed that there was no noticeable change in the charge distribution of an electrified smoke on aging but that the particles in an originally uncharged smoke gradually built up charges with time. Whytlaw-Gray and Patterson (1932) have clarified the mechanisms for the two cases. Considering first a highly charged smoke, such as one of magnesium oxide, it is evident that a charge will only be neutralized and an uncharged particle produced when particles carrying equal and opposite charges aggregate. The probability of such a collision depends upon the range of charges present in the smoke, and since a magnesium oxide smoke exhibits a wide range of sizes and of charges, the chance of a contact producing a neutral particle is quite small. Hence, aggregation would not be expected to change appreciably the fraction of particles charged, and the same degree of electrification would persist for extended periods of time.

The behavior of an originally uncharged aerosol, such as ammonium chloride produced with the LaMer generator, is quite different from that of a highly charged smoke. If an aerosol is uncharged initially, it can become charged by capturing ions from the air. The increase in the number of charged particles depends, therefore, on the extent of the natural ionization of the surrounding medium. Gradually the number of electrified particles increases, although the magnitude of the charge is small, and multiple charges on a particle are rare in the early stages of aging.

b. Artificial. The experimental results showed that an uncharged aerosol of ammonium chloride could be rapidly electrified by exposure to the ionized atmosphere about a radioactive source. Approximately half the particles of the ammonium chloride aerosol became charged
when the aerosol was passed over the radioactive source. Most of the charged particles carried only a unit charge, however. Little change in the charge distribution of a magnesium oxide aerosol (charged by thermal emission at the time of generation) was evident after the aerosol had aged in the presence of a radioactive source. This result may be explained on the basis of the random distribution of the charged particles in the aerosol and of the random charging by the air ions resulting from the radiation, i.e., a particle, whether charged or not and whether charged negatively or positively, if charged, is about as likely to pick up a positive as a negative ion.

C. Aerosol Aggregation

1. Sedimentation Technique

The sedimentation of aerosol particles afforded a means for studying some aspects of the aerosol's behavior. Figure 7 shows that the settling rate of an ammonium chloride aerosol was unchanged by the electrification of the aerosol, although the shape of the aggregates had changed somewhat. The shape of the charged and uncharged ammonium chloride particles, given in Figure 8, indicates that the tendency for chain-like aggregates was greater when the particles were charged. Thus, it appears that although the electrical charge had no appreciable effect in increasing aggregation, the orientation of the particles comprising an aggregate is dependent on charge. Whytlaw-Gray and Patterson (1932) also found that charging had no effect on the aggregation of aerosol particles. Gillespie (1952), however, studying larger particles with much greater charges, found the aggregation rate to be increased as the charging was increased.
Light-scattering measurements as conducted in this investigation indicated a possibility of a small degree of aggregation. These measurements were quite sensitive. However, in the case of the sedimentation measurements, as well as in light-scattering work, the shape of the aggregate may have had more effect on the degree of aggregation.

The experimental results on the sedimentation rate in the presence of various vapors show that the settling rates of both magnesium oxide and ammonium chloride aerosols were increased by the presence of water vapor and reduced by the presence of propylene glycol vapor. As shown in Figure 12, the aggregates of magnesium oxide particles in a humid atmosphere appear to be more compact and dense than the dry aggregates and, hence, would be expected to settle faster. The aggregates in an atmosphere of propylene glycol also appear to be more compact than the dry aggregates, and, on that basis alone, would be expected to settle faster than the dry aggregates. Closer examination of the aggregates in the propylene glycol atmosphere shows that there are more small, discrete groups than in a dry atmosphere. Since from Stokes' law the terminal settling velocity is proportional to the square of the diameter, it follows that, on the basis of size, the magnesium oxide aggregates in the presence of propylene glycol would settle at a slower rate, the result which was detected experimentally.

Since ammonium chloride is hygroscopic, it was necessary to consider the growth of a particle in various humidities. Calculations by the method of Neiburger and Wurtele (1949) show that the diameter of an ammonium chloride particle is not greatly changed until very humid conditions are reached. For example, an ammonium chloride particle with a normal
diameter of 0.22 micron would increase to 0.23 micron in an atmosphere of 40 per cent relative humidity; 0.25 micron at 50 per cent relative humidity; and 0.47 micron, more than double the original size, at 90 per cent relative humidity. Hence, it seems that the large increase in sedimentation rate at humidities of 40-50 per cent cannot be attributed to an increase in size of the constituent particles but rather to the formation or shape of the aggregates. This conclusion was, in general, borne out by electron photomicrographs. Ammonium chloride particles settled more slowly in a propylene glycol atmosphere than in an ordinary, dry atmosphere, yet aggregate formation was evident from the analysis of the sediment. Further clarification of this effect is necessary since it appears that there may be a change in the effective density of the aggregates. As Whytlaw-Gray and his associates have pointed out, many aggregates contain pockets of occluded air which effectively lower the density of the clumps, leading to slower settling rates. The recent studies of Artemov (1947) describe the influence of vapors on the shape of aggregates and the effect of particle shape on the aggregation rate. It is interesting to note that this same investigator, Artemov (1946), had stated earlier that foreign vapors have no effect on aggregation and that contrary data are due to errors of technique. In addition to a possible relation between particle shape and sedimentation rate, the shape of a particle influences the light-scattering properties of the aerosol.

The purpose of the sedimentation studies, discussed above, and the light-scattering studies, discussed in the following section, was to elucidate the mechanism of aggregation and the effect of various vapors on aggregation. The latter problem has received much attention in recent years. Indeed, a survey of the literature reveals far more disagreement than corroboration.
Smirnov and Solntseva (1938) report the effectiveness of water vapor and butyric acid as aggregants for an ammonium chloride aerosol, but Samokvalov and Kozhukhova (1936) state that water and octyl alcohol in low concentrations act as stabilizers, rather than aggregants, for ammonium chloride. Samokvalov (1937) suggests that if the vapor of a substance with a high dipole moment is introduced into a nonpolar medium such as air, the polar substance undergoes oriented adsorption on the dispersed particles and thus stabilizes the dispersion. Radushkevich and Chugunova (1938) have found that the rate of coagulation of an ammonium chloride aerosol was reduced by phenol and was unaffected by methyl alcohol, ethyl alcohol and oleic acid. Tikhomirov, Tunitskii and Petryanov (1941) report that phenol vapors had no effect on the aggregation of a ferric oxide aerosol.

Many of the discrepancies in published experimental work may be traced to different methods of investigation. For example, in several of the references cited the foreign vapor was introduced before or at the time of aerosol generation, whereas in the present study the vapors were introduced after the generation of a dilute and relatively stable aerosol. At the present time, evidence obtained at certain conditions on certain aerosol systems may not be applied directly to other systems and conditions.

2. Dynamic Technique

Calculations for ammonium chloride particles and tungsten light, using a publication of the National Bureau of Standards (1949), show that aggregation of an aerosol whose individual particles are less than 0.75 micron in diameter would increase the light-scattering power of the aerosol until the diameter of the particles exceeded about 0.75 micron. The particles of the ammonium chloride aerosols used in this study had a mean
diameter of about 0.22 micron, and all of the other aerosols exhibited average particle diameters smaller than 0.5 micron. Since the vapor itself produced no measurable light scattering, the increased scattering in the presence of the aerosol particles could be attributed either to (1) particle growth as a result of the adsorption of the vapor, (2) particle aggregation or to (3) a changed scattering effectiveness of the particles because of vapor adsorbed on their surfaces.

The growth of the particles in humidities of the magnitude employed seems to be so small as to be quite insignificant. This effect was discussed in the preceding section. The possibility of a change in scattering action because of a change in the humidity of the air about aerosol particles was investigated. A tiny glass rod with small ammonium chloride crystals stuck on it was mounted in the light-scattering chamber in such a way that a light beam played on the crystals and some of the scattered light was picked up by a phototube. It was found that wide relative humidity changes (between 30 and 80 per cent) produced no measurable change in the amount of light scattered. Indications from the light-scattering portion of this investigation are therefore strong that aggregation of the aerosol particles was the principal result of the vapors in many cases. In general, this was borne out by electron photomicrographs of aerosol particles collected from the various vapors.

The greatest aggregation found was that produced by water vapor and an aerosol of ammonium chloride. This result is probably explained by the mechanism suggested in the section on "Theoretical Considerations." That is, ammonium chloride, being hygroscopic, causes the water molecules to be less in number near each ammonium chloride aerosol particle than in the
main body of the air, resulting in a somewhat reduced pressure in the vicinity of the particles and making it somewhat easier for two particles to collide.

Light-scattering measurements indicated that propylene glycol also increased the aggregation rate of ammonium chloride particles, but this was contradicted by sedimentation studies. How this situation will eventually be resolved is not known; however, great differences in the packing of aggregates have been observed and demonstrated (see Figures 8, 12 and 13), and the solution may eventually be found to lie in this fact. It is probable that a loosely packed aggregate, while settling slowly, would scatter light differently from a tightly packed aggregate which would settle relatively rapidly.

The fact that most of the aerosols listed in Table III were unaffected by the vapors tested can generally be explained in accordance with the vapor pressure theory outlined in the "Theoretical Considerations" section of this report.

The effect of electrical charges on the aerosol particles is uncertain from light-scattering measurements probably because the shape and tightness of the aggregates must again be considered.

3. Counting Studies

The particle-counting apparatus has given results which showed a consistent response to aerosol concentration over a wide range of concentrations. Since the counter was developed to provide an accurate measure of the absolute particle concentration, extensive work has been devoted to calibration of the instrument. Because the counter operates on the principles of light scattering, it is necessary to consider the
light-scattering effectiveness of the material comprising the aerosol particles when determining the lower limit of countable size. The apparatus is now regarded as capable of giving concentration data at higher concentrations and for smaller particles than the instrument described by Cucker and O'Konski (1949). It can still be improved.

Calibration of the counter has been attempted by comparison with microscopic analyses of a sample of the aerosol. Aerosol particles for counting with a microscope were obtained with a thermal precipitator. In the case of the aerosols of Serratia marcescens bacteria, the fact that the particle count by the counting apparatus was lower than the value calculated from the concentration of the bacteria in the liquid suspension may be the result of either (1) a classifying action in the nebulizer (DeVilbiss No. 40) from which the aerosol was generated, or (2) a decrease in the number of viable bacteria through the action of the nebulizer, since it has been suggested that only the viable bacteria remain large enough to be counted with the apparatus. In the case of the clay aerosols, the particle concentrations given by the counter were probably as indicative of the true concentration as the counts by the microscopic technique. It appears probable, therefore, that a counter may be used to evaluate the aggregation of aerosols.
VI. CONCLUSIONS

As noted elsewhere, the literature reveals many cases of apparent disagreement concerning aerosol behavior. Because of this discord, many of the results of this work, while serving as confirmation of some studies, also serve as refutation of other studies. Therefore, it is necessary to qualify most of the following conclusions as pertaining only to the materials and conditions employed in the present work.

1. The ultimate or "equilibrium" electrification of aerosol particles is a function of the particle size. That is, the magnitude of the charge carried by an aerosol particle apparently increases roughly as the surface area increases.

2. The shape of aggregates of aerosol particles is related to the electrical charge carried by the particles. Charged particles showed a pronounced tendency to form chain-like clumps or groups, suggesting polarization, while aggregates of uncharged particles exhibited more random clumping.

3. Electrification, in the degree attained by the charging methods employed and by the natural ionization of the atmosphere, is of minor importance in the aggregation of an aerosol. The sedimentation rate of an aerosol was unchanged by charging the particles, and the light-scattering measurements showed only a slight change, a part of which was probably due to aggregation.

4. The effect of electrification on aggregation has not been clearly distinguished from the effect on the shape of the aggregate. Since aggregation, sedimentation rate and light scattering are all affected by the shape of the particles, it is necessary to examine the effect of par-
ticle shape on the methods of aggregation measurement (sedimentation, light-scattering) before assessing any effects on the aggregation process itself.

5. The charge-analyzing apparatus developed in this work affords a convenient and rapid measure of the degree of an aerosol's electrification.

6. Some vapors change the aggregation rates of certain aerosols, as evidenced from sedimentation and light-scattering measurements in conjunction with electron photomicrographs. The particular influence of the vapor depends on the aerosol system and the nature of the vapor; at present there is little information upon which accurate predictions can be made regarding the degree or type of influence, e.g., aggregation or stabilization. Recent studies, however, indicate that substances which lower the vapor pressure of the suspended particles increase the probability of collision by removal of the "vapor cushion" surrounding a particle.

7. Aerosols of liquid droplets or of bacteria are more susceptible to the actions of vapors than are aerosols of inert solid particles. This comes about because the interactions of liquid or bacterial aerosols are conditioned by the vapor pressure of the individual droplets or particles.

8. An apparatus for electronically counting the number of particles in an aerosol is believed capable of development for use in concentration studies.
VII. RECOMMENDATIONS

During the course of the present research project it has become apparent that several aspects of the problem justify further study and, in addition, that investigation of new areas of interest is necessary to clarify certain phases of the research work.

Aerosol generation is commonly accomplished by atomizing a volatile liquid containing the finely divided aerosol material; by atomizing a nonvolatile liquid, by vaporizing and condensing either a solid or a liquid, or by dispersing a dry powder. In each of these cases, the most rapid clumping or aggregation of the individual aerosol particles occurs near the point of generation of the aerosol because it is here that particle concentration, turbulence and other factors are greatest.

Being particularly attentive to aggregation near the point of generation, it is recommended that information be obtained on the aggregation of aerosols—primarily bacterial aerosols—in relation to: (1) the type of atomizer, spray nozzle or other form of disseminator employed, (2) the electrification of the aerosol, (3) changes in atmospheric conditions and (4) conditions prior to dissemination.

Respectfully submitted:

M. DallaValle,
Project Director

Clive Orr, Jr.,
Research Engineer

Approved:

Herchel H. Cudd, Acting Director
Engineering Experiment Station
VIII. APPENDIX
BIBLIOGRAPHY

ARTEMOV, I.S.,

------
1947 "Effect of the Particle Shape on the Rate Constant of the Coagulation of Aerosols." Kolloid Zhur. 2, 225-30.

CUNNINGHAM, E.,

DALLAVALLE, J. M.,

------, ORR, C., JR., AND WOODWARD, L. A.,

EASTMAN KODAK COMPANY,

EINSTEIN, A.,

FEDOSEEV, V. A., MANAKIN, B. A., AND DOMENTIANOVA, Z. M.,

GIBBS, W. E.,

GILBERT, H. W., AND SHAW, P. E.,

GILLESPIE, T.,

GUCKER, F. T., JR., AND O'KONSKI, C. T.,
HARNWELL, G. P.,

HAUSER, E. A., AND LYNN, J. F.,

KOLTHOFF, I. M., AND STENGER, V. A.,

KUNKEL, W.,

KUNKEL, W.,

KUNKEL, W., AND HAIJEN, J. W.,

LAMER, V. K.,

LAMER, V. K.,

NATIONAL BUREAU OF STANDARDS,

NEIBURGER, M., AND WURTELE, M. G.,

PATerson, H. S., WHYTlAW-GRAy, R., AND CAWOOD, W.,

PETRYANOV, I. V., TIKHOMIROV, M. V., AND TUNITSKII, N. N.,

RADUSHKEVICH, L. V., AND CHUGUNOVA, O. K.,
SAMOKVALOV, K.,

----, AND KOZHKHOVA, O. S.,

SINCLAIR, D.,

SMIRNOV, L. V., AND SOLNTSEVA, V. A.,

SMOLUCHOWSKI, M.,

TIKHOMIROV, M. V., TURITSKII, N. N., AND PETRYAHOV, I. V.,

WELLS, P. V., AND GERKE, R. H.,

WHITE, L., AND HILL, D. G.,

WHYTTLAW-GRAY, R., AND PATTERSON, H. S.,
Figure 22. Optical Density Curve Showing the Charge Distribution on Tobacco Smoke in the Presence of Ammonium Vapor.
Figure 23. Optical Density Curve Showing the Charge Distribution on Tobacco Smoke in the Presence of Propylene Glycol Vapor.
Figure 24. Optical Density Curve Showing the Charge Distribution on Tobacco Smoke in the Presence of Methyl Alcohol Vapor.
Figure 25. Optical Density Curve Showing the Charge Distribution on Tobacco Smoke in the Presence of Water Vapor.
Figure 26. Optical Density Curve Showing the Charge Distribution on an Ammonium Chloride Aerosol.
Figure 27. Upper Block: The Effect of Salt Ions in an Atmosphere of 40 Per Cent Relative Humidity on Light Scattered from Ammonium Chloride Aerosol. Lower Block: The Effect of Water Vapor on Light Scattered by Dry Air in the Absence of Aerosol.
Figure 28. The Effects of Organic Vapors on Light Scattered from Ammonium Chloride Aerosols.
Figure 29. The Effects of Organic Vapors on Light Scattered from Ammonium Chloride Aerosols.
Figure 30. The Effects of an Organic Vapor and Salt Ions on Light Scattered from Ammonium Chloride Aerosols.
Figure 31. The Effects of Nitrobenzene on Light Scattered from Ammonium Chloride Aerosols.
Figure 32. The Effects of Water Vapor and Organic Vapors on Light Scattered from Propylene Glycol Aerosols.
Figure 33. The Effects of Organic Vapors and Salt Ions on Light Scattered from Propylene Glycol Aerosols.
Figure 34. The Effects of Organic Vapors and Water Vapor on Light Scattered from Stearic Acid Aerosols.
Figure 35. The Effects of Organic Vapors on Light Scattered from Stearic Acid Aerosols.
Figure 36. The Effects of Organic Vapors and Salt Ions on Light Scattered from Stearic Acid Aerosols.
Figure 37. The Effects of an Organic Vapor and Salt Ions on Light Scattered from β-Naphthol Aerosols.
Figure 38. The Effects of Water Vapor and Organic Vapors on Light Scattered from β-Naphthol Aerosols.
Figure 39. The Effects of Organic Vapors on Light Scattered from β-Naphthol Aerosols.
Figure 40. The Effects of Water Vapor and Some Organic Vapors on Light Scattered from Tin Chloride Aerosols.
Figure 41. Effect of β-Radiations on the Aggregation of an Ammonium Chloride Aerosol as Indicated by Light Scattering.