

REPORT No. 38.

AIRPLANE DOPES AND DOPING.

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HISTORICAL.

Cellulose acetate and cellulose nitrate are the important constituents of airplane dopes in use at the present time, but planes were treated with other materials in the experimental stages of flying. The above compounds belong to the class of colloids and are of value because they produce a shrinking action on the fabric when drying out of solution, rendering it drum tight. Other colloids possessing the same property have been proposed and tried. In the first stages of the development of dope, however, shrinkage was not considered. The fabric was treated merely to render it waterproof.

The first airplanes constructed were covered with cotton fabric stretched as tightly as possible over the wings, fuselage, etc., and flying was possible only in fine weather. The necessity of an airplane which would fly under all weather conditions at once became apparent. Then followed experiments with rubberized fabrics, fabrics treated with glue rendered insoluble by formaldehyde or bichromate, fabrics treated with drying and nondrying oils, shellac, casein, etc. It was found that fabrics treated as above lost their tension in damp weather, and the oil from the motor penetrated the proofing material and weakened the fabric. For the most part the film of material used lacked durability.

Cellulose nitrate lacquers, however, were found to be more satisfactory under varying weather conditions, added less weight to the planes, and were easily applied. On the other hand, they were highly inflammable, and oil from the motor penetrated the film of cellulose nitrate, causing the tension of the fabric to be relaxed. The film does not possess the objectionable brittleness of glue or casein, and, in general, this type of dope had much in its favor.

About the year 1910, the Bayer Co., of Elberfeld, Germany, began to exploit a type of cellulose acetate known as Cellit for use on airplanes. This material had been used in the preparation of a noninflammable celluloid called Cellon. Experiments were made with thin sheets of Cellon, which were fastened to the fabric to protect it, and this suggested the use of cellulose acetate in solution. In 1910, acetate dopes were used and found to produce a satisfactory shrinkage, and to be proof against water, oil, and gasoline. Such dopes were more expensive than nitrate dopes, but the noninflammability of the acetate film caused a slow but general adoption of cellulose acetate solutions. At the present time such dopes are considered the best for use on aircraft.

Dopes are also used on balloon fabric to reduce the permeability of the fabric to gas. The English Government uses Delta dope for this purpose, a nitrate dope containing sufficient castor oil to make it nonshrinking. The Navy Department has used Delta dope on certain airships, on which the fabric had become too permeable to gas, and satisfactory results were obtained. The use of acetate dopes on balloons is receiving consideration.

COMPOSITION OF DOPES.

A dope consists of the cellulose ester dissolved in suitable solvents to which diluents are added, with the addition of plastics and a compound to neutralize the traces of acidity in the solvents, or the acidity which may develop in the film. The solvent contains a compound of

high boiling point which allows the cellulose ester to emerge from the solvent mixture in a transparent condition, free from precipitated cellulose ester which appears in the film in streaks or spots. The development of such whitened areas is known as "blushing." It results from the application of dope in a humid atmosphere, or from the rapid evaporation of low-boiling solvents and diluents, or both. In the presence of a high-boiling solvent, the moisture has a chance to evaporate before the film is dry, and the cellulose ester is not precipitated. The amount of the "high boiler," as it is frequently called, depends upon its boiling point. If the latter is high, less of the compound is needed than when it is low. Solvents with boiling points between 125° and 200 C. are generally used. A high-boiling diluent may be present in nitrate-dopes to assist in the prevention of blushing.

Diluents generally consist of mixtures of alcohols and hydrocarbons, and frequently denatured alcohol and benzene are used.

Plastics are occasionally used in nitrate dopes, but are always present in acetate dopes. The nitrate film has sufficient inherent strength and elasticity without further modification, but a small amount of castor oil or camphor is sometimes incorporated in it. Acetyl cellulose, however, is inherently brittle and certain softening bodies or plastics must be added to it in order to impart suppleness and increase its life. A plastic is frequently a solid of low melting point, sometimes a liquid or a mixture of liquids, and generally a solvent of the cellulose ester with which it forms a solid solution. A small amount of the "high boiler" is always left in the dope film, and this also plasticizes it. A suitable base is generally present in the film to neutralize acidity. The base commonly used is urea.

CELLULOSE NITRATE DOPES.

Cellulose nitrate or guncotton is produced by the nitration of cotton or some form of cellulose approximating the degree of purity of cotton. For dopes a low nitrated cotton is desirable. It must be stable in order that no decomposition with development of acidity may occur. The high boiler in nitrate dopes is generally amyl acetate or butyl acetate. The former is a product of fusel oil and the latter is prepared from butyl alcohol, a by product in the production of acetone by fermentation. The diluent is generally a mixture of denatured alcohol and benzene, although methyl alcohol, methyl acetone, and xylol are also employed. A low-boiling solvent, such as ethyl acetate, may be also present. The solvent and diluent combination used in nitrate dopes is influenced by the degree and method of nitration, and therefore is subject to considerable variation.

CELLULOSE ACETATE DOPES.

The manufacture of cellulose acetate is a technical art, demanding careful supervision and control. Variations of a few degrees of temperature during the process have an adverse effect upon the product. The correct preparation of the material is known only to a few chemists. It is quite difficult to make two batches of the ester alike, and frequently there is trouble in spite of efforts to keep the quality uniform. The material is a white solid, its appearance depending upon the method employed for its precipitation. A good cellulose acetate has an asbestos-like quality when rubbed between the fingers.

At the outbreak of hostilities in this country, dopes were prepared from scrap acetate film. These dopes did not give results in service, which should be expected of cellulose acetate. The film scrap was frequently old stock, and contained plastics. In the preparation of dope it was dissolved in suitable solvents with the addition of dope plastics. On this account the dope film was frequently overloaded with softening agents.

The commonest "high boiler" used in this country in acetate dopes is diacetone alcohol, a product of acetone obtained by condensation in the presence of lime. In Germany, before the war, ethyl lactate was the "high boiler" in common use. This substance has a tendency to break up into ethyl alcohol and lactic acid unless certain compounds are added to it to make it stable. Methyl ethyl ketone in suitable amount also prevents blushing, but not as effectively as the preceding compounds, unless a considerable amount is present. In this connection it

may be pointed out that a suitable proportion of alcohol and benzene, when present in the dope, removes much of the moisture present. A certain mixture of alcohol, benzene, and water has a higher vapor pressure than any of its constituents, and when this mixture results during evaporation water is readily removed. Acetone oils are also used as high boilers, but the composition of these oils varies greatly; and, because they may break up with the development of acidity unless carefully purified, they have not found as much favor as compounds of known purity.

Solvents are usually acetone, methyl acetate, methyl acetone, tetrachlorethane, and ethyl formate. Acetone has not been used during the period of hostilities because it has been needed in the preparation of cordite and for other purposes. The preparation of methyl acetate involves less consumption of acetate of lime than the production of acetone, and hence has been preferred because its use conserves raw material. Methyl acetone is a product of the destructive distillation of wood. It is largely a mixture of acetone and methyl alcohol, and when the latter is acetylated, water removed, and acid present neutralized, a good solvent results. The composition of methyl acetone varies considerably, and sometimes it is necessary to increase its solvent power by the addition of methyl acetate or acetone. Tetrachlorethane was formerly a favorite solvent in acetate dopes. It combines the functions of a solvent and plastic and dissolves cellulose acetates of a wide degree of hydration. However, its vapor has been shown to be about four times as toxic as that of chloroform and unless pure it decomposes and causes deterioration of the fabric. The vapor of the compound causes jaundice, and in England several fatalities resulted in the application of dopes containing it. The decomposition of tetrachlorethane can be prevented by the use of suitable pigments, and the danger attending its application could be nullified if all doping rooms were provided with adequate means of ventilation. Unfortunately, ideal conditions of ventilation do not exist, and one by one, the allies have all abandoned the use of tetrachlorethane dopes. France and Italy have even ruled out dopes containing chlorine in any form.

Ethyl formate has not been used in the United States but is allowed by the British Government. It is an excellent solvent.

Diluents commonly used are denatured alcohol and benzene, sometimes methyl alcohol, either added as such or present in methyl acetone. Cellulose acetate dissolves in a mixture of alcohol and hydrocarbon when warmed and is reprecipitated in the cold, but the solubility persists in the presence of a solvent of cellulose acetate such as acetone. When the ratio of hydrocarbon to alcohol is three to one, an increased amount of diluent may be used.

The plastics which have been proposed for use in acetate dopes include many compounds, some of which are much superior to others. Benzyl alcohol is used by the British Government. Mixtures of eugenol and triacetin have found favor in France. In this country, the commonest are phenyl salicylate, which is an excellent softener, mixtures of benzyl benzoate and benzyl acetate, benzyl acetate alone, and triacetin. Triacetin is water soluble, and may decompose with the liberation of acetic acid. Triphenylphosphate is in universal use in acetate dopes. It waterproofs and fireproofs the film, and is an excellent softener. When used in excess, however, triphenylphosphate softens in warm weather and makes the acetate film soggy. Urea is used in small amount to neutralize any free acid which may be present.

DOPE COVERS.

The dope, as has been previously mentioned, protects the fabric, keeping it taut, so flying is possible under all weather conditions. It is also necessary to protect the dope film by covering it with some suitable coating containing pigments to exclude light rays. Either pigmented dopes or varnish enamels are used for this purpose. It has been conclusively proven by Dr. Ashton, attached to the Royal Aircraft Factory, that the deterioration of dopes is practically entirely caused by sunlight. His results show that the curve of the intensity of sunlight and the curve of deterioration of doped fabrics are almost identical. It is therefore more feasible to use a pigmented dope or a pigmented wood-oil varnish, rather than clear dope or varnish as a dope cover. Clear varnish has until recently been used in this country on Army planes.

The Navy has used a gray, pigmented varnish enamel. Dr. Ramsbottom, also attached to the Royal Aircraft Factory, has recently demonstrated that doped fabrics covered with pigmented dope retain their tautness longer than similar fabrics covered with an enamel. He also demonstrated that a pigmented dope retains its tautness best of all, and that such a dope effects a considerable saving of cellulose acetate. The English Government for a long time has used a type of pigmented dope, khaki colored by iron pigments and lampblack, which is called P. C. 10. It is a nitrate dope containing the pigments and sufficient castor oil to reduce to a minimum the shrinkage ordinarily effected by a dope. Reports from the front indicate that the use of such a cover has been attended by excellent retention of the tautness and durability over a long period, and Dr. Ramsbottom's suggestion regarding pigmented dopes therefore merits serious consideration.

APPLICATION OF DOPES.

In the application of dopes to fabrics, it should be remembered that the fabric does not of itself shrink in the sense that mercerization causes shrinkage. In other words, there is no physical change occurring in the fabric. The dope film contracts when drying out of solution and diminishes the space between the threads, the total effect of which is slightly to reduce the original area of the fabric. The British Government at one time used a dilute solution of dope next to the fabric. This was called a scratch coat. The dope contained very little softening agent and produced maximum shrinkage. The scratch coat, however, was found to reduce the tear resistance of the fabric and was, therefore, abandoned. Such a coating penetrates the fabric very thoroughly and locks the fibers and threads. It is apparent that the viscosity of the dope must permit of some penetration, so that the dope will not peel off, but the penetration must not be excessive. The amount of size in the fabric to some extent influences penetration. The first coat of dope is well worked into the fabric and subsequent coats are flowed over it, care being taken not to go over a given area more than once or twice, or the doping brush will drag on the dope film. Sufficient dope is applied to produce a weight increase of 2 to 2.5 ounces per square yard. The Army specifications require four coats of dope on all planes, and specify nitrate dope on training planes and acetate dope on combat planes. Two coats of clear varnish or enamel are applied over the dope.

The Navy Department specifies two coats of acetate dope over the fabric, followed by three coats of nitrate dope and two coats of navy-gray enamel. The inflammable nitrate dope is thus laminated between the relatively fire-resistant acetate dope and the enamel, the pigment in which also affords resistance to fire. It has been contended that the use of one type of dope above the other may produce two films of different physical properties, but to date no trouble has been experienced by the Navy in the durability of dopes applied as above.

FIREPROOFED DOPES.

Inasmuch as nitrate dope is comparatively cheap and acetate dope expensive, numerous attempts have been made to reduce the inflammability of the nitrate film. This has been attempted by fireproofing the fabric or dope or both. Fireproofing is generally effected in one of three ways—by encasing the material in a coating of inert mineral salts, by using compounds which decompose with the liberation of a gas which checks combustion, or by incorporating an organic fireproofing compound in the dope film.

Any compound used for checking the spread of combustion should not dissociate with an acid or alkaline reaction in the presence of moisture, as acids, particularly mineral acids, attack the fabric, and alkalis have a saponifying action on cellulose esters and certain plastics. A great variety of fireproofing solutions for fabrics and fire-resistant dopes have been submitted to the Bureau of Standards for examination. The best treatment for fabrics has been found to be a 10 per cent solution of ammonium phosphate neutralized with ammonia. This has been found to exert no deleterious action on fabric or dope. Soluble chlorides in general have been found to weaken the fabric.

Several pigmented fireproofed dopes have been examined. The pigments used have consisted of finely ground ammonium phosphate or magnesium ammonium phosphate. These are incorporated in suitable proportion in a fine state of division in a nitrate dope. The dope is applied alternately with clear dope, one coat of pigmented dope on the fabric, then clear dope, then pigmented, etc. five coats in all. A pigmented varnish is applied over the dope.

Several fireproofed dopes resembling an English product called "titanine dope" have also been submitted. These consist of nitrate dopes containing chlorides of zinc, calcium, or magnesium added in alcoholic solution. The hygroscopicity of these salts is objectionable, and such dopes tend to become slack on the fabric in humid weather. This can be overcome in part by laminating the dopes between coats of clear dope.

Nitrate dopes may also be fireproofed by incorporating tricresylphosphate or hexachlorethane in the dope film. The former compound is preferable and forms a better solid solution with cellulose nitrate than triphenylphosphate. It is necessary to fireproof the fabric when dopes of this type are applied.