Investigation of Heat Stabilizers for Nitrocellulose Film

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A major consideration in formulating nitrocellulose coatings and films for any application is the thermal aging characteristics of the material (apart from photochemical sensitivity). The resistance of nitrocellulose to degradation and embrittlement during relatively short periods of aging at elevated temperatures is notoriously low. Reviews are available on the degradation and stabilization of nitrocellulose (*2*, *15*).

The development of purification treatments in the manufacture of nitrocellulose has led to improvements in its stability. Even so, chemical stabilizers are frequently incorporated in nitrocellulose formulations to prolong the life of the product. Although considerable work has been done to determine the effects of additives on stability, the available information is usually concerned with denitration and gas evolution, but seldom with ability to prevent changes in physical properties that occur with aging. The present work was undertaken to determine the effect of more than 40 selected organic compounds on the heat stability of nitrocellulose film at 160° F., taking into account changes in physical properties, and to some extent to study the relationship of molecular structure of the additives to degradation.

The decomposition of nitrocellulose is generally considered to proceed in two stages. In the first stage, it occurs spontaneously at a slow rate which is temperature-dependent and negligible at room temperature, and produces nitrogen oxides; in the second, it proceeds at an accelerated rate due to an autocatalytic effect which the first-stage decomposition products exert on further polymer degradation. There is evidence (*27*) to support the belief that nitrogen dioxide is formed by the homolytic cleavage of the weak O_2N—O link as the first step in the decomposition of nitrocellulose (*1*, *15*, *17*, *18*). Two types of radical centers may thus arise: one at the original secondary nitrate site, the other at the primary nitrate site. It was suggested that in the former case the adjacent nitrogen dioxide is eliminated while homolytic carbon-carbon bond cleavage occurs, producing two aldehyde groups (*17*, *27*); in the latter case, formaldehyde is eliminated producing a new radical center adjacent to the ring oxygen; this intermediate is capable of rearrangement to form an aldehyde group with chain cleavage (*26*, *27*). Another radical center may form on the carbon atom adjacent to the glucosidic oxygen by abstraction of hydrogen by other radicals; this intermediate might rearrange with homolytic chain cleavage and formation of a keto group (*26*, *27*). Aldehydes are thus formed which are capable of converting NO_2 to NO (*15*, *18*).

In the second stage of the decomposition, acids which result from interaction of the nitrogen oxides with the water present cause hydrolytic chain scission and hydrolysis of nitrate groups (*2*). Another source of nitrocellulose instability closely related to the second-stage decomposition is traces of nitrating acid which may be retained by the nitrocellulose because of incomplete neutralization at the time of manufacture. Furthermore, the unstable half ester of sulfuric acid with nitrocellulose which forms during nitration, if not neutralized, readily hydrolyzes to give sulfuric acid which is capable of initiating the autocatalytic decomposition.

Although it is generally believed that no known substance can reduce the first-stage homolytic decomposition, further degradation may be prevented if nitrogen oxides and hydrogen ions can be removed (*2*, *15*). A stabilizer usually consumes nitrogen dioxide and nitric acid by nitration reactions. It is incorporated with the nitrocellulose to remove the first-stage decomposition products as soon as they are formed, and thereby prevent the accelerated decomposition of the second stage. For taking up residual acids, slightly alkaline stabilizers are useful.

Chain cleavage, however, will be catalyzed by the stabilizer itself, if sufficiently basic. The most widely accepted mechanism of this behavior is that ether linkages beta to the electronegative carbonyl groups are activated toward alkaline cleavage (*10*, *14*, *15*). [The carbonyl groups may arise via the initial spontaneous decomposition, by the oxidation of glucose units (*14*), or by the oxidation-reduction reaction in which nitrogen dioxide is removed with alkali (*3*, *15*).] Inductively, the carbonyl group causes hydrogen on the alpha-carbon atom to be alkali-labile. Upon removal of this proton by base, a double bond forms between the alpha- and beta-carbon atoms by an electron-pair shift, and the beta-ether linkage simultaneously cleaves heterolytically.

A large number of stabilizing additives have been proposed, of which weak organic bases are most widely used. These include diphenylamine, 1,3-diethyl-1,3-diphenylurea (centralite-1) and 1,1-diphenylurea (acardite) (*2*). Other proposed compounds, which serve to indicate the wide variety of substances which have been investigated, are phenanthrene, polybasic acids such as tartaric acid, amyl alcohol, *N*,*N*-dimethylaniline, cyanoguanidine, carbazole, *N*,*N*′-diphenylbenzidine, and triphenylamine (*15*). Oxidation inhibitors have been observed to retard degradation in one investigation of aging effects in solution (*25*), but not in another (*6*). While peroxides hasten decomposition, the role of oxygen in the degradation of nitrocellulose is considered to be minor, except that it oxidizes NO to NO_2 which can be absorbed by the stabilizer or which will catalyze the decomposition in the absence of a stabilizer (*15*, *23*).

A method widely used for determining the chemical stability of nitrocellulose is the 134.5° C. heat test (*11*) in which the nitrocellulose is considered to be in an acceptable state of preservation if it does not discolor methyl violet paper when heated at 134.5° C. for a prescribed period of time. Tests of this nature which are based on the evolution of nitrogen oxides do not necessarily relate to such physical properties of nitrocellulose film as impact strength and flexibility. Although heat stability tests detect oxides of nitrogen, they do not necessarily indicate degree of chain degradation. For example, nitrocellulose which does not appear to evolve excessive amounts of nitrogen oxides may be undergoing extensive physical deterioration. An additive might appear to retard the evolution of oxides of nitrogen by chemically absorbing them, but cause chain scission itself by its own acidic or basic nature.

Viscosity measurements of solutions of aging nitrocellulose film were used for following the course of degradation in this study. Because the intrinsic viscosity of nitrocellulose is affected by the degree of nitration (*12*) such that loss of nitrogen dioxide causes a viscosity decrease, and a lowering in viscosity also reflects any polymer degradation taking place, a change in viscosity might indicate either or both effects. Assuming that any viscosity decrease is undersirable, an additive holding this decrease to a minimum was considered a good stabilizer.

PROCEDURE

An industrial grade of alcohol-wetted, 5 to 6-second, nitrocellulose with a nitrogen content of 11.8 to 12.2%, originating in three containers of a single, 2-year-old lot (lot 1) was used, unless otherwise specified. The remainder was taken from two containers of a fresh lot (lot 2).

The additives investigated were Eastman Kodak Co. White Label, or the equivalent except for the following: *p-tert*-butylphenol, 2,5-di-*tert*-butylhydroquinone, 2,6-lutidine, *o*-methoxyphenol, 2-nitrodiphenylamine, and *N*-nitrosodiphenylamine which were practical grade; 4,4′-dihydroxybenzophenone and *N,N′*-diphenyl-*p*-phenylenediamine which were technical grade. Technical grade methyl ethyl ketone (2-butanone) was distilled before use.

Films, 10 × 15 inches, approximately 0.010 inch thick were cast from solutions prepared in the following manner: Approximately 20% by weight of dry nitrocellulose was dissolved in methyl ethyl ketone. The additive was dissolved in a small amount of the solvent and thoroughly blended with the nitrocellulose solution. The amount of the additive, unless otherwise specified, was 1% by weight of the dry nitrocellulose. The films were cast from solutions which had been allowed to stand no longer than 24 hours at room temperature.

The films were cast on glass plates by drawing the poured solutions down to uniform thickness with an adjustable knife edge using a wooden frame to guide the knife. The coated plates were allowed to dry at room temperature for 24 to 72 hours in a level position, covered with glass plates about 1/4 inch above the surface to obtain bubble-free films by retarding solvent evaporation. Care was taken to exclude drafts in order to avoid film blush. The films were then stripped from the plates and allowed to dry by suspending them for one week at room temperature exposed to free air circulation. Sections, 1 × 6 inches, were cut from the films and more solvent was removed in a desiccator under reduced pressure (aspirator) for 24 to 72 hours at room temperature. The film strips were then placed in glass beakers and aged in a mechanical convection oven at 160° ± 2° F.

Deterioration was measured by change in viscosity and was determined as follows: A solution was prepared of 1.0000 to 1.0005 grams of the aged film strip in 100 ml. of methyl ethyl ketone, and the kinematic viscosity was determined for the fresh solution at 25° ± 0.1° C. For each additive, viscosity measurements of fresh solutions of aged film were taken over a minimum aging period of 24 weeks at the following times: zero time, 72 hours, 1, 2, 4, 8, 12, 16, 20, and 24 weeks. For certain additives, because the slope of the viscosity curve was in doubt, the aging period for the film was extended and viscosity measurements were taken also at 28 weeks and at 4-week intervals thereafter.

In general, throughout the study (except in the case of some additives which immediately accelerated degradation), there was an initial increase in viscosity indicating in part, at least, that residual solvent had been driven off at the aging temperature, 160° F. The viscosity-degradation curves were extrapolated to zero time (as in Figure 1) to obtain approximately true initial viscosities.

DEGRADATION OF NITROCELLULOSE FILM

The nitrocelluloses without additives varied noticeably in stability from container to container, although they originated from the same lot of material. Figure 1 shows the viscosity decrease of solutions of aged nitrocellulose film in the absence of an additive. The nitrocellulose was taken from lot 1 which had been stored in the "cotton" form under ambient, but probably different conditions for 2 years before being used. The aging of the films of nitrocellulose from containers 2 and 3 was begun 6 and 10 months, respectively, after that from container 1. The aged film from container 1 evidenced brittleness at 12 weeks of aging, but until 20 weeks the film from container 2 showed no signs of embrittlement. The material from container 3 was flexible at 12 weeks and brittle at 16 weeks.

The data in Figure 2 show that the degradation rate is not reproducible when samples of nitrocellulose are taken for accelerated aging at different times from the same container. The nitrocellulose samples were taken from a single container from lot 2 which had been standing at room temperature. The accelerated aging of film B was begun approximately 5 months after film A; films C and D followed 3 months after film B. The curves show that the longer the material stood at room temperature, the faster it deteriorated at the elevated temperature. Although the fresh nitrocellulose was stable at elevated temperature, the material was less stable at elevated temperature after aging a relatively short time (5 months) at room temperature. After storage for 8 months at room temperature, the material degraded rapidly at elevated temperature. The curves for duplicate films C and D illustrate that degradation curves can be reproduced reasonably well when samples of the same material are aged concurrently under the same conditions.

Variations in the stability of different samples of initially uniform nitrocellulose toward deterioration at elevated temperature depended upon both the age of the materials and differences in conditions of environment to which they were exposed prior to accelerated aging (such as storage at varying distances from heat). Variations in initial viscosities and degradation rates, attributable to the latter, are shown in Figure 1.

RELATIVE STABILIZING EFFECTIVENESS OF ADDITIVES

The relative effectiveness of an additive toward the stability of nitrocellulose film was determined by comparing its viscosity-degradation curve to that for diphenylamine, one of the most widely used stabilizers for nitrocellulose propellants. In making the comparisons, factors such as initial drop, height, and slope of the curves were considered. Because of the differences existing among containers of nitrocellulose, diphenylamine curves determined for the nitrocellulose originating in each container of lot 1 were used as reference levels enabling comparisons to be made of the stabilizing effects of additives tested with material from different containers. The stabilizing effect of recrystallized diphenylamine can be seen by comparing Figure 3 with Figure 1. (Recrystallized and unrecrystallized diphenylamine gave the same results.) The films represented in Figure 3 were still flexible after 32 weeks of aging. The levels of the extrapolated initial viscosities in Figure 3 are close, respectively, to the corresponding extrapolated levels in Figure 1, which was generally true for all good stabilizing additives. That is, for a given container of nitrocellulose, the initial viscosity level did not vary to any great extent whenever an effective stabilizer was present (see Figures 5 and 10 to 12). On the other hand, there were several compounds for which initial viscosities were at considerably lower levels because of an accelerated degradation due to the presence of the compounds.

Aromatic Amines. In the series of aromatic amines represented in Figure 4, generally those compounds containing no primary amino groups and no more than one amino group to a benzene ring, as diphenylamine and *N,N′*-diphenylbenzidine, are the most effective stabilizers. Benzidine, 1-naphthylamine, *N,N′*-diphenyl-*p*-phenylenediamine, and *p*-phenylenediamine are less effective, and of these, *p*-phenylenediamine, having two primary amino groups on the one ring, is at the lowest level. As expected, the more basic amines are among those producing the low-level curves.

Figure 5 shows the effect of various *N*-substitutions in diphenylamine and aniline. *N*-nitrosodiphenylamine is more effective than diphenylamine, while triphenylamine and 1,1-diphenylurea are roughly equivalent to the same compound; *N,N*-diphenylformamide has little or no stabilizing action toward nitrocellulose film although the compound has been used as a stabilizer for propellants (*19*). Ethyl carbanilate is slightly more effective than diphenylamine; ethyl-*N*-ethyl carbanilate, another stabilizer sometimes used in propellants (*19*), has little or no stabilizing effect. Acetanilide, an effective stabilizer, is about equivalent to *N,N′*-diphenylbenzidine (Figure 4); *N,N′*-diphenylethylenediamine behaved in a similar manner to *N,N′*-diphenyl-*p*-phenylenediamine (Figure 4). Introducing a nitro group in the 2-position of diphenylamine

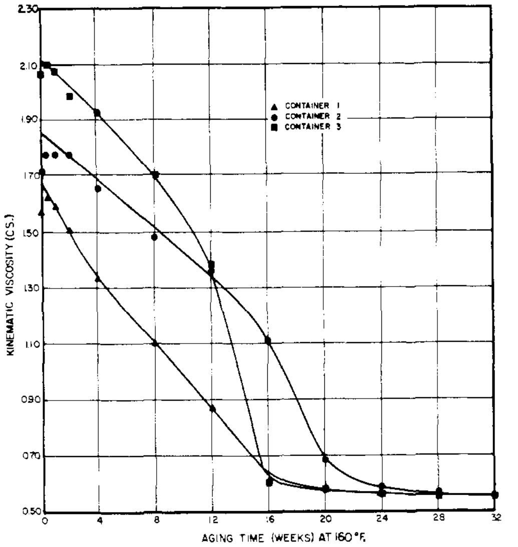

Figure 1. Thermal degradation of nitrocelluloses originating in three containers of a single lot

caused a slight increase in effectiveness over diphenylamine (see also Figure 10) while bonding the rings at the 2,2′-positions, as in carbazole, caused a small decrease. The latter compound was apparently exhausted after 36 weeks of aging.

Phenols. The effect of some substituted phenols is shown in Figure 6. Compounds substituted in the para, or an ortho position with groups which lead to high electron-density in the ring are generally good stabilizers equal to, or better than diphenylamine. They include methoxy-, phenyl-, and *p*-*tert*-butylphenols, *p,p′*-biphenol, and *p*-benzyloxyphenol (although this compound was exhausted beyond 24 weeks). 4,4′-Dihydroxybenzophenone, in which the carbonyl group is expected to be electron-withdrawing, *m*-methoxyphenol, and phenol itself are less effective. Resorcinol is about equivalent to diphenylamine, and is more effective than phloroglucinol and phenol. The degradation curves for some substituted *o*-methoxyphenols indicate that further ring substitutions as in vanillin and eugenol cause no increase in stabilizing activity, and that in the case of 2,6-dimethoxyphenol, there is a definite detrimental effect (see also Figure 10).

2,5-Di-*tert*-butylhydroquinone (Figure 6), which approaches diphenylamine in effectiveness, cannot be assumed to stabilize

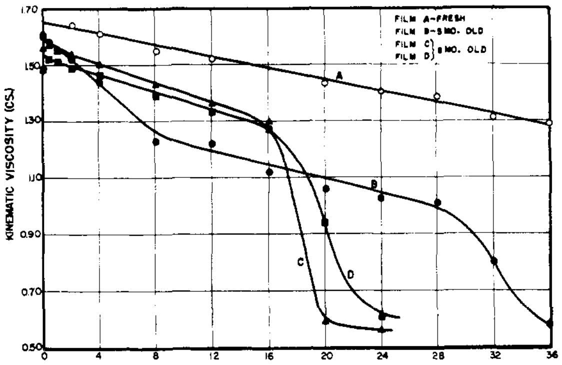

Figure 2. Varying effect of age of nitrocellulose on the accelerated aging of films

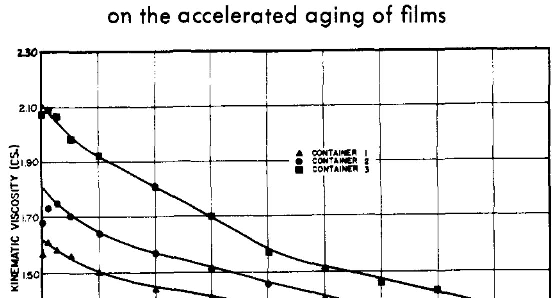

Figure 3. Stabilizing effect of diphenylamine on nitrocelluloses from three containers of a single lot

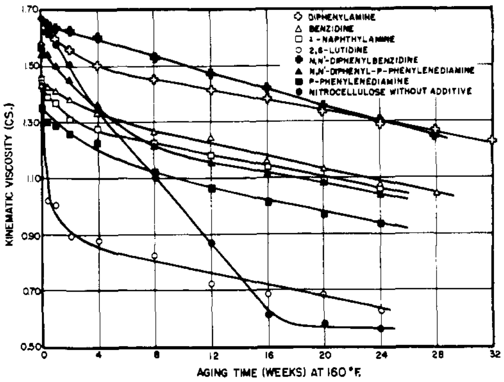

Figure 4. Effect of aromatic amines on the heat stability of nitrocellulose film

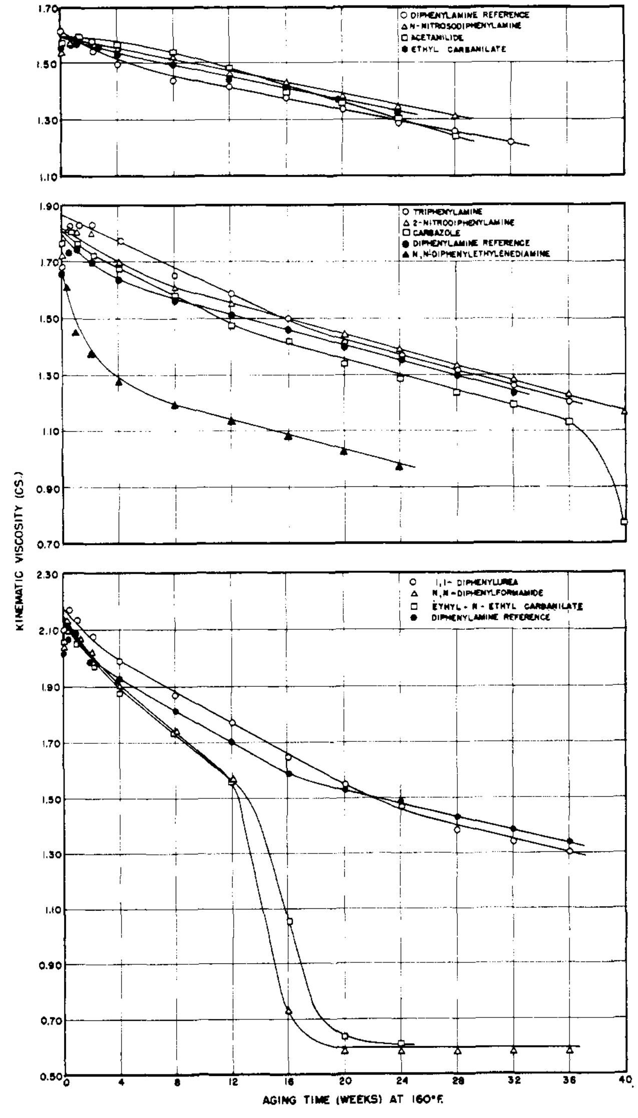

Figure 5. Effect of some ring- and *N*-substituted diphenylamines and anilines on the heat stability of nitrocellulose film

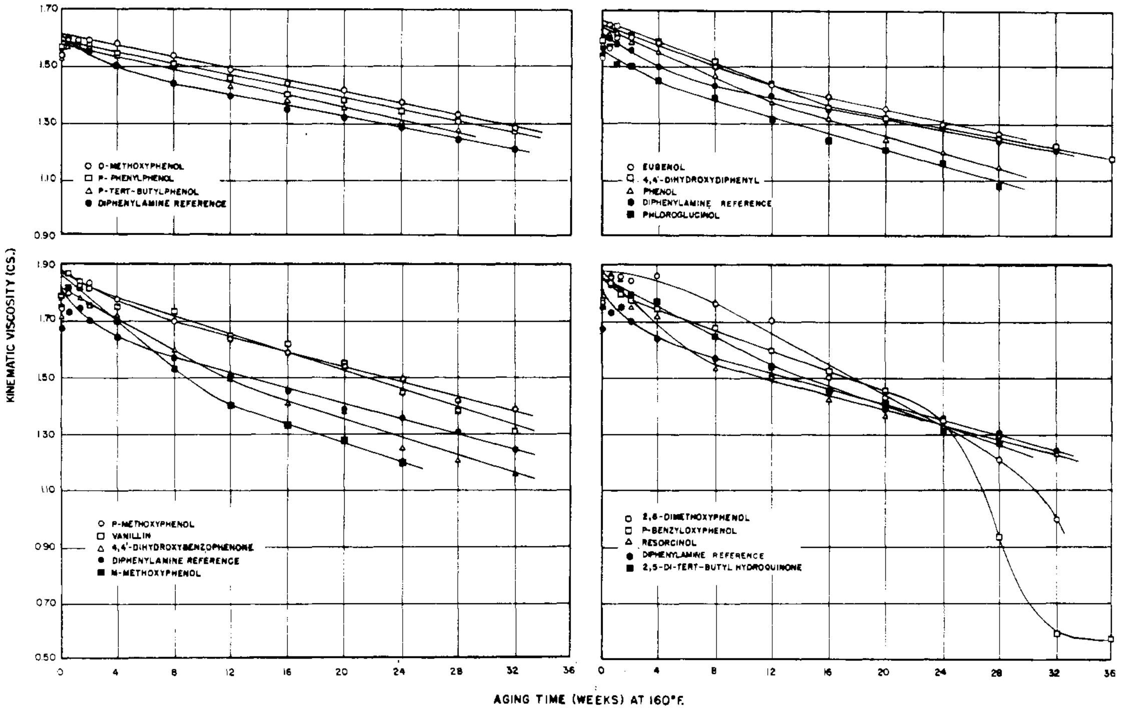

Figure 6. Effect of some substituted phenols on the heat stability of nitrocellulose film

solely by taking up nitrogen dioxide because the bulky *tert*-butyl groups sterically hinder ortho-nitration (*5*). Although the presence of a reducing agent like hydroquinone might effectively suppress the alkaline decomposition which results in the formation of a carbonyl group at the site of the nitrate group (*3*, *13*), and thus prevent further degradation by alkaline cleavage, it is unlikely that 2,5-di-*tert*-butylhydroquinone did so, because alkali was absent. It is possible that this compound stabilizes via free radical inhibition. Such stabilization, in particular, prevention of bond cleavage with lowering of chain length by a compound that inhibits a radical chain process, cannot be ruled out.

Ureas and Related Compounds. Figure 7 shows the degradation curves for some substituted ureas and related compounds with their corresponding diphenylamine reference curve. 1,3-Dimethyl- and 1,3-diethyl-1,3-diphenylureas are about equivalent to diphenylamine; 1,3-diphenylurea is less effective. 1,1-Diphenylurea, shown in Figure 5, is about as effective as diphenylamine. Furthermore, 1,3-diphenylurea, 1,5-diphenylcarbohydrazide, and 1-phenylsemicarbazide are nearly equivalent to each other (Figure 7). They are superior to related thio compounds which lead to embrittlement and, invariably, insolubilization of the nitrocellulose in methyl ethyl ketone. Highly alkaline 1,3-diphenylguanidine, as expected, is inferior to 1,3-diphenylurea.

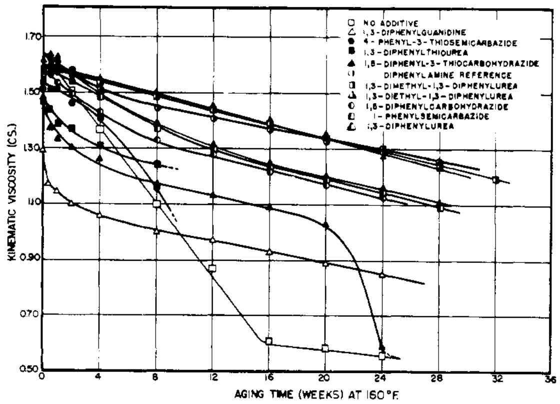

Figure 7. Effect of some substituted ureas and related compounds on the heat stability of nitrocellulose film

Mixed Stabilizers. The effect of combining two stabilizers was studied briefly to see whether the presence of the second stabilizer would improve upon the stabilizing effect of the first.

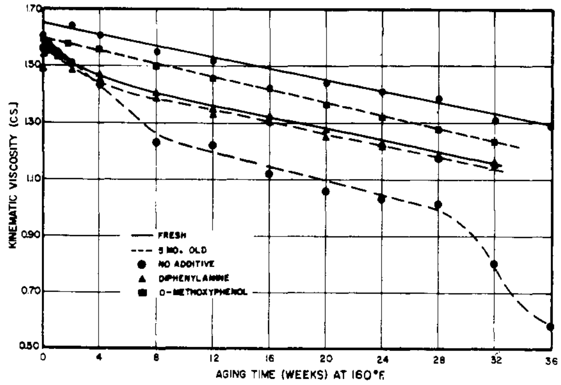

Figure 8. Effect of diphenylamine and o-methoxyphenol on the accelerated aging of films cast from fresh and five month old nitrocelluloses taken from a single container

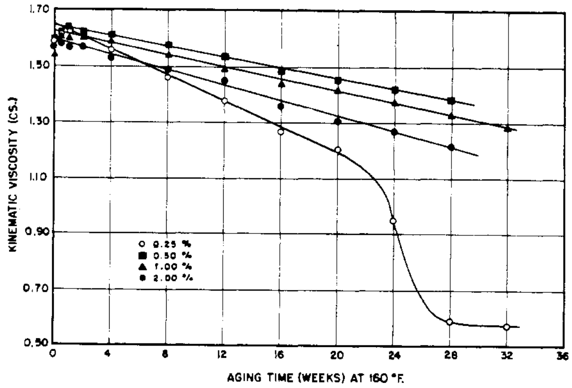

Figure 9. Effect of increasing the concentration of o-methoxyphenol

The degradation curves for ethyl carbanilate (Figure 5) and *o*-methoxyphenol (Figure 6) separately are parallel to the curve for diphenylamine. In Figure 10, the degradation curve for the mixture of ethyl carbanilate and *o*-methoxyphenol (each at 1%) is seen to parallel the curve for diphenylamine for two different containers of nitrocellulose. While the slope for 2% *o*-methoxyphenol was greater than for 1% (Figure 9), the slope for the combination of 1% *o*-methoxyphenol and 1% ethyl carbanilate (totaling 2%) was identical to that for 1% *o*-methoxyphenol. Further work is necessary to explain this behavior. Perhaps it is more advantageous to incorporate a second stabilizer rather than increase the concentration of a single stabilizer to obtain a longer service life for nitrocellulose film.

ACCELERATED BREAKDOWN BY ADDITIVES

In some cases additives had a considerable deleterious effect causing the nitrocellulose to degrade even sooner than in the absence of an additive. Compounds such as 2,6-lutidine, 1,3-diphenylguanidine, and *p*-phenylenediamine (Figures 4 and 7) which are relatively strong bases obviously induced degradation immediately after their incorporation into the films. The low levels of these degradation curves indicated advanced states of deterioration and that these additives accelerated degradation: The film containing 2,6-lutidine was brittle at 8 weeks; the film containing 1,3-diphenylguanidine was very nearly brittle at 24 weeks. A noticeable transition from a state of flexibility to an obvious state of brittleness always occurred below 0.90 centistoke, and brittleness was particularly evident in those films whose solution viscosities had decreased to the vicinity of 0.70 centistoke. (For the three unstabilized nitrocelluloses whose degradation curves are shown in Figure 1, brittleness was observed at times corresponding to this viscosity range.) By obvious embrittlement is meant that the film crumbled readily on handling, and at times was in a highly crazed condition. The transition from flexibility to brittleness was observed superficially by simply pinching the doubled films between two fingers and noting whether they cracked. For all containers and lots of nitrocellulose, whenever degradation proceeded unchecked, the minimum viscosity reached was always in the vicinity of 0.55 centistoke under the conditions of the study, indicating that the ultimate products of degradation were of the same molecular size. The kinematic viscosity for methyl ethyl ketone alone under the same conditions was 0.50 centistoke.

The leveling of the lower curves in Figures 4 and 7, as with 2,6-lutidine, 1,3-diphenylguanidine, and *p*-phenylenediamine, indicates that the base-catalyzed rapid degradation was finally held in check (but not a familiar slow degradation), and probably occurred because the basicity of the compounds decreased as the nitration reaction proceeded. Some derivatives, therefore, which formed as a result of interaction with the nitrocellulose decomposition products are probably good stabilizers. *N*-Nitrosodiphenylamine and 2-nitrodiphenylamine are slightly more effective than diphenylamine in stabilizing nitrocellulose film. Similarly, *N*-nitroso and nitro derivatives of a compound such as *p*-phenylenediamine would be expected to be less basic, hence possible effective stabilizers.

Diphenylamine and carbazole are presumably capable of attack on nitrocellulose (*7, 8*), but the degradation rate when catalyzed by diphenylamine is much slower than that catalyzed by the nitrocellulose decomposition products (*8*). An example of a deleterious behavior of diphenylamine is also seen in this work. Figure 8 shows the effect of diphenylamine on a fresh, originally stable sample of nitrocellulose film (lot 2). Diphenylamine in the sample produced a curve whose height was considerably lower than the curve for a second sample aged concurrently without an additive. It appears that the lower level of the former curve was largely due to a small viscosity decrease, most of which took place within the first 4 weeks of aging.

o-Methoxyphenol was particularly prominent in not appearing to cause an initial viscosity drop (Figures 8, 9, and 13), and for that reason was better than diphenylamine as a stabilizer. Figure 8 shows practically no adverse behavior of *o*-methoxyphenol toward the originally stable nitrocellulose other than a slight increase in slope. Other compounds of similar behavior were *N*-nitrosodiphenylamine and ethyl carbanilate (Figure 5), *p*-phenylphenol, and *p*-*tert*-butylphenol (Figure 6). Acetanilide (Figure 5), *N,N'*-diphenylbenzidine (Figure 4), and 1,3-dimethyl- and 1,3-diethyl-1,3-diphenylureas (Figure 7) were others, although their slopes were generally steeper than that of diphenylamine.

STABILIZATION AND THE SLOW RATE OF DEGRADATION

Throughout the work one general slope predominated in the degradation curves for most of the additives. The slow degradation represented by this slope indicated that most of the compounds sooner or later opposed at least the rapid degradation attributed to the autocatalytic effect of the nitrocellulose decomposition products—i.e., nitrogen oxides and acids—upon further chain degradation.

This slope undoubtedly manifests the inherent, slow degradation which, presumably, cannot be reduced. The constant recurrence of this slow degradation, indicating a continuous process of denitration and chain cleavage (the latter attributable to a free radical, nonchain process), reflects the inability of the additives (including those considered to be effective stabilizers) to prevent it, even though they may prevent the degradative effect attributed to the products of denitration. (Radical inhibitors should be effective stabilizers to the extent that denitration leads to chain cleavage via a radical-chain process.) However, for all practical purposes, a compound may be considered an effective heat stabilizer if it prevents the rapid degradation (allowing or causing only a minimum, initial, rapid degradation at most) though it does not inhibit the slow decomposition.

Although the slow degradation presumably operates independently of any additive, in the case of *o*-methoxyphenol, a strong stabilizing additive, the slow rate of degradation varied with concentration (Figure 9). As the content of the additive was increased from 0.5 to 2.0%, the slope of the aging curve increased slightly, indicating an increasing rate of degradation. At 0.25%, although a certain amount of stabilization was obtained, the additive was soon exhausted, whereupon the nitrocellulose decomposed rapidly. The optimum concentration for *o*-methoxyphenol appears in the vicinity of 0.5% in this particular instance.

The slow rate of degradation did not vary to any great extent with most of the additives at the 1% concentration used. However, small differences in slope evident in some cases in Figures 4 to 7 might be eliminated through small adjustments in concentration of the additives. Thus *N,N'*-diphenylbenzidine may be far more effective than diphenylamine (Figure 4) on a weight basis. Decreasing the concentration of *N,N'*-diphenylbenzidine to some figure less than 1% should cause a decrease in the slope of the curve if an analogy to the behavior of *o*-methoxyphenol can be drawn. This may also be true of compounds such as acetanilide (Figure 5), and 1,3-dimethyl- and 1,3-diethyl-1,3-diphenylureas (Figure 7).

STABILIZATION BY FREE RADICAL INHIBITORS

The homolytic removal of nitrogen dioxide in the decomposition of nitrocellulose might produce several radical intermediates capable of leading to chain cleavage via free radical chain processes. If the decomposition of nitrocellulose can be induced by such free radicals, it seems reasonable that the addition of free radical inhibitors should decrease the rate of decomposition. Thus, 2,5-di-*tert*-butylhydroquinone may stabilize by removing such radicals.

Stabilization via radical inhibition must not be overlooked in view of the relatively low concentration at which the additives were used. Several of the amino compounds—e.g., diphenylamine—and substituted phenols used are radical inhibitors. Besides reacting appreciably with the nitrocellulose in an unknown manner, and producing compounds of unknown nature, the amino compounds (and presumably the phenols) are being nitrated in stabilizing nitrocellulose (*20–22*). Aromatic nitro compounds (including nitrophenols and nitroaromatic amines) are important as a class of chain terminators for vinyl polymerization (*9*, *24*). In the case of the solvent-induced chain decomposition of benzoyl peroxide, nitrobenzenes are good inhibitors and nitrophenols such as *p*-nitrophenol and picric acid are strong retarders (*4*, *16*). The retarding effect of the nitrophenols is mainly due to the nitro groups (*4*). Returning to the case of nitrocellulose, the inhibitors, upon being nitrated, may become even more reactive chain terminators. This may partly account for the increased effectiveness of 2-nitrodiphenylamine over diphenylamine and the leveling of the curves in Figure 4 (the other factor being decreased basicity).

Probably because it was unable to take up nitrogen dioxide, 2,5-di-*tert*-butylhydroquinone was not among the best stabilizers (Figure 6). Other phenols, such as *o*- and *p*-methoxy- and phenyl-, may have been superior because they were capable of being nitrated in addition to their inhibiting radicals. (However, the presence of these compounds in greater molar concentration than 2,5-di-*tert*-butylhydroquinone may partly account for their greater effectiveness.) Apparently when used in nonexcessive amounts, the best heat stabilizers for nitrocellulose are weakly basic, neutral, or weakly acidic compounds which have a high capability of being nitrated, and are good free radical inhibitors at the same time. Thus it might be advantageous to use a combination of two stabilizers; one, a polynitro compound, the other, a compound for undergoing nitration.

GENERAL APPLICABILITY OF STABILIZERS

Additives which stabilized the nitrocellulose from one container, stabilized the nitrocellulose from other containers of the same lot or different lots. 2-Nitrodiphenylamine stabilized the nitrocellulose from both the second and third containers of lot 1, as did a mixture of ethyl carbanilate and *o*-methoxyphenol (Figure 10). (The reversal in the relative positions of the curves for the mixture, and for 2-nitrodiphenylamine in going from one container to the other, emphasized that where there were only small differences in the heights of the curves, differences in effectiveness between additives were probably insignificant.) *p*-Methoxyphenol stabilized the nitrocellulose from the second container as effectively as *o*-methoxyphenol stabilized the material from the first container, as indicated when comparisons are made with the diphenylamine curves (Figure 11). The two isomers were equivalent, as expected. Furthermore, *o*- and *p*-phenylphenol are about equivalent when compared to their respective diphenylamine curves; these stabilized the nitrocellulose from the third and first containers, respectively (Figure 12). Also, *o*-methoxyphenol stabilized the nitrocellulose from the first container of lot 1, and also the relatively fresh nitrocellulose from container 2 of the second lot (Figure 13). Figure 10 shows similarity in the behavior of 2,6-dimethoxyphenol, a compound not considered to be a particularly good stabilizer, to the nitrocellulose originating in containers 2 and 3.

From inspection of Figures 10 to 13, it appears that stabilizing additives have the effect of eventually equalizing the degradation rates of all containers and lots of 5 to 6-second nitrocellulose, regardless of previous history. As a corollary it can be stated that the slow rate of spontaneous degradation tends to be the same under identical aging conditions regardless of the previous history of 5 to 6-second nitrolcellulose. That is, given two samples of nitrocellulose from the same or different lots, which have the same initial viscosity except that one degrades much faster than the other at elevated temperatures, then a stabilizing additive, used at the same concentration in each, will tend to produce curves which coincide; or given two samples which have different initial viscosities, then the additive will produce curves which tend to become parallel. Figure 8 also bears out the foregoing generalizations; diphenylamine had practically an identical effect on fresh and 5-month-old samples of nitrocellulose which were taken from the first con-

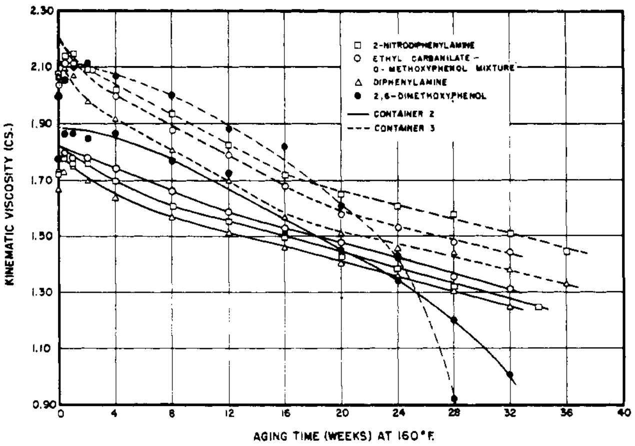

Figure 10. Effect of additives on nitrocelluloses originating in two containers of a single lot

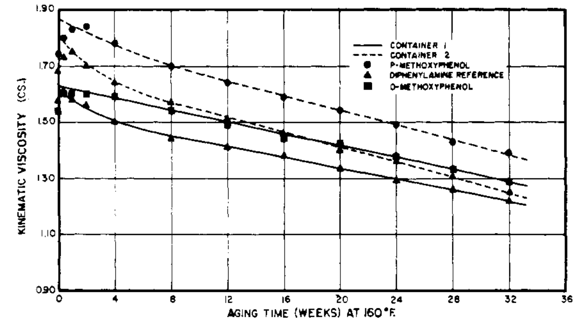

Figure 11. Equivalent stabilizing effects of ortho and para isomers of methoxyphenol

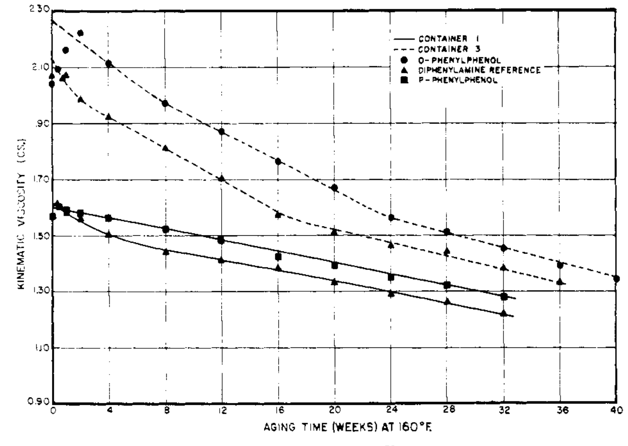

Figure 12. Equivalent stabilizing effects of ortho and para isomers of phenylphenol

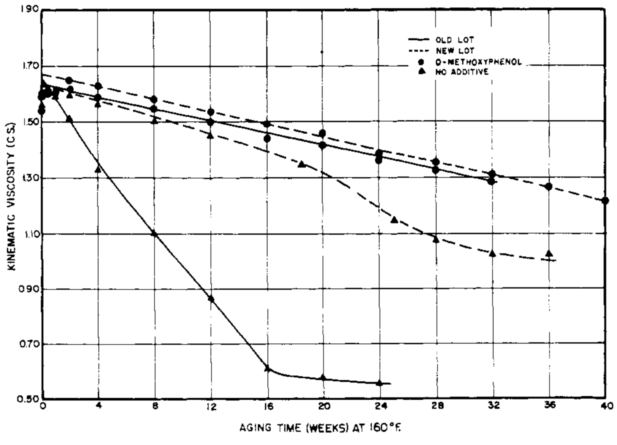

Figure 13. Stabilizing effect of o-methoxyphenol on nitrocelluloses taken from old and new lots

tainer of lot 2. [A characteristic shape seemed to prevail in the degradation curves for a given container of nitrocellulose whenever the material was effectively stabilized (Figures 10 and 12).]

The spontaneous decomposition of nitrocellulose is retarded when the temperature is reduced so that degradation at room temperature is negligible. The evidence in Figure 8 indicates also that the extent of nitrocellulose chain degradation during room-temperature storage is negligible or only very slight (because the diphenylamine curves were practically identical). The curves for nitrocelluloses without an additive, as in Figures 1 and 2, reflected the presence of accumulated decomposition products.

An increase in the amount of these products degrades the nitrocellulose very little at room temperature; however, the degrading effects of the increasing accumulation are intensified at elevated temperatures, resulting in increasing rates of degradation the older the sample before aging at elevated temperature, as shown in Figure 2. By incorporating a stabilizer, however, the decomposition products are removed and the nitrocellulose is thus stabilized. The longer the nitrocellulose has aged at room or ambient temperatures, the more rapidly it will degrade at elevated temperature in the absence of a stabilizer. However, if a stabilizer is incorporated before aging the nitrocellulose at elevated temperature, then the room-temperature age is not very important, except that the additive may be exhausted sooner the older the nitrocellulose, because of the presence of larger quantities of decomposition products. Until that happens, a stabilizer apparently will reveal the same slow degradation rate at elevated temperature regardless of previous history in the case of 5- to 6-second nitrocellulose.

A stabilizer can have a deleterious effect on a fresh sample of nitrocellulose which is originally stable—e.g., diphenylamine in Figure 8. This effect, if small, is minor compared to the amount of stabilization which is potentially available because of the presence of the additive. While the diphenylamine-stabilized nitrocellulose will continue to degrade at the same slow rate (until the stabilizer is exhausted), the unstabilized nitrocellulose is liable to degrade suddenly at a rapid rate as seen in the lowest curve of Figure 8. Contrary to the general rule (*2*) that no stabilizer should be used except in the case of smokeless powder, the advantage to be gained by incorporating a nonexcessive amount of a heat stabilizer in nitrocellulose film is obvious.

SUMMARY AND CONCLUSIONS

The viscosity decrease of solutions of aging nitrocellulose film with time was taken as an indication of the degradation rate of the nitrocellulose (reflecting both the loss of nitrogen dioxide and decrease in chain length) as influenced by the presence of the additive.

Most of the additives sooner or later inhibited the rapid degradation, although none inhibited the inherent, slow nitrocellulose decomposition. The slow rate of degradation occurring in the presence of a stabilizer tended to be the same regardless of the previous history of the nitrocellulose. In the absence of an additive, previous storage conditions and age were factors in the stability of the nitrocellulose toward deterioration at elevated temperature, but the addition of stabilizers virtually eliminated these effects. Relatively strongly basic compounds caused considerable initial degradation probably via base catalysis; to some small extent this occurred with a good stabilizer like diphenylamine. Some derivatives which formed as a result of the interaction of these compounds with the nitrocellulose decomposition products are probably good stabilizers. *N*,*N*-Diphenylformamide and ethyl-*N*-ethyl carbanilate, compounds which have been used as nitrocellulose propellant stabilizers, had little or no stabilizing effect on nitrocellulose film.

The following compounds are effective heat stabilizers for nitrocellulose film, in the decreasing order shown based on a 1% use concentration (Because near neighbors may not differ significantly, reference should also be made to the figures): *o*- and *p*-methoxyphenol, *o*- and *p*-phenylphenol, *N*-nitrosodiphenylamine, 2-nitrodiphenylamine, ethyl carbanilate, vanillin, *p*-*tert*-butylphenol, eugenol, *p*,*p*'-biphenol, triphenylamine, acetanilide, *N*,*N*'-diphenylbenzidine, 1,3-dimethyl-1,3-diphenylurea, 1,3-diethyl-1,3-diphenylurea, 1,1-diphenylurea, diphenylamine, resorcinol, 2,5-di-*tert*-butylhydroquinone, and carbazole.

As a class, the substituted phenols are at least as effective as aromatic nitrogen-containing stabilizers. The effectiveness of 2,5-di-*tert*-butylhydroquinone is explained on the basis of radical chain inhibition.

When used in nonexcessive amounts, the best heat stabilizers for nitrocellulose are weakly basic, neutral, or weakly acidic compounds which have a high capability of being nitrated, and are good free radical inhibitors at the same time. An effective heat stabilizer for nitrocellulose film prevents the rapid degradation encountered at elevated temperature (allowing or causing only a minimum initial, rapid degradation at most) even though it does not inhibit the inherent, slow nitrocellulose decomposition. A small, initial deleterious effect upon fresh nitrocellulose is minor compared to the amount of stabilization which is potentially available because of the presence of a nonexcessive amount of the stabilizer.

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