## Novel Self-Crosslinking Epoxy Oligomers for Cationic-Cure Coatings Applications

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# Novel Self-Crosslinking Epoxy Oligomers for Cationic-Cure Coatings Applications

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*Novel epoxy functional oligomers containing phosphate-esters, carboxylate-ester, and urethane linkages with varying molecular weight and functionality have been synthesized from commercially available epoxy compounds. These oligomers are characterized for the parameters relevant to the study by physical, spectroscopic, and chemical methods. Two series of cationic thermal-cure coating compositions have been formulated using these oligomers as principal film-forming components. The cured films of these self-crosslinked oligomers have been studied and compared. A correlation between structure of these oligomers and their film properties has been established.*

## INTRODUCTION

Organic coatings are important materials and vital to host of industries such as automotive, metal containers, coil sheet and strip, wood furniture, machinery and equipment, metal furniture and fixtures, electrical and electronics, among others. Without coatings, these

manufacturers would not be able to produce vehicles, appliances, equipment, and furniture as appealing, enduring, or marketable as they can today. Although the coating industry constantly keeps pace in developing new products and providing services, over the last several years the major driver for this development has been regulatory and environmental needs, mainly the compliance with the Volatile Organic Compounds (VOC) regulations [1–2].
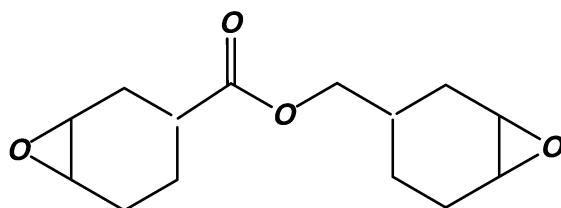
Over the past several years, the coating industry has developed technologies and products that not only address these challenges but also improve cost and efficiency. Some of the important technologies developed include water-borne coatings, powder coatings, high-solid coatings, and radiation-cure coatings. The products based on these technologies have been commercialized and used in a wide range of end use applications [3].

One of the important areas of development of the new generation coatings is to employ a suitable crosslinking technology. In general, crosslinking reactions, often referred to as curing reactions, involve chemical reactions between the functional groups (or reactive sites) present on crosslinkers and/or the base polymers, leading to the formation of crosslinked matrix of film. Crosslinking brings about significant change in physical, chemical, and mechanical properties of the coatings [4,6]. It has been well established that the performance properties of the convertible coatings can be tailored by suitable polymer architecture and crosslink density, among other factors. One important consideration is designing these coatings to achieve a desired degree of crosslinking in an efficient manner [7].

Depending on the resin chemistry, the crosslinking reactions are initiated and brought about by a variety of means such as free-radical initiation, catalysis, or using external agents such as moisture or oxygen. The cure efficiency and the performance properties of these coatings are significantly affected by the type and amount of initiators or catalysts used, and the cure conditions. One of the methods used for initiating the curing reaction involves generation of cationic species, which catalyze the cure reactions. This method is commonly known as, and herein after referred to as "cationic curing."

In general, the cationic curing coating systems involve oxirane functional polymers (or oligomers), a chemical compound capable of producing a relatively stable and efficient cationic species (cationic catalyst) and hydroxyl functional co-reactants and modifiers. The reaction is initiated by generating cations by the action of heat (thermal cationic systems) or UV-radiation (UV cationic systems). A simplified schematic representation of cationic cure mechanism is shown in Figure 1.

**FIGURE 1** A simplified cationic-cure reaction scheme.

The cationic cure coating systems offer several benefits over other curing methods. The distinct advantages include low temperature cure, lower shrinkage, and hence better adhesion, no air inhibition, dark cure, low odor, and low skin irritancy and good self stability. Despite these benefits, the growth of cationic cure system over the past several years has been very sluggish. The reasons for this slow growth are mainly: (a) Limited chemistry—the systems invariably have to be epoxy based, which limits their applications; (b) sensitivity to moisture or other basic materials—moisture present in the atmosphere or the presence of basic pigments significantly retard curing rates as they interfere with cations; (c) poor wetting and adhesion properties—due to the absence of polar groups that help in substrate wetting, pigment wetting, and adhesion. A careful examination of these factors reveals that many of the limitations are associated with the chemical structure of the polymeric materials, and that by suitable molecular architecture these limitations can be controlled or overcome.

**Epoxidized Soybean Oil (ESO)**



**3,4-Epoxycyclohexyl-3,4-epoxycyclohexane carboxylate**

**FIGURE 2** Starting epoxy compounds used to synthesize oligomers.

In the present work, a series of novel epoxy functional oligomers, suitable for cationic curing, based on varying chemistries have been synthesized from Epoxydized Soybean Oil (ESO) and a commercial cycloaliphatic epoxy compound (3,4-epoxycyclohexyl-3,4-epoxycyclo-hexane carboxylate). Figure 2 shows the chemical structures of these epoxy compounds. These oligomers have been characterized and formulated into coating composition. The properties of cationic ther-mally cured films of these systems have been studied and compared. An attempt has been made to establish a correlation between the chemical structure of the oligomers and the film properties.

## EXPERIMENTAL

## Materials

ESO with 6.9% oxirane oxygen content (VIKOFLEX 7170) was procured from ATOFINA. The cycloaliphatic diepoxide compound 3,4-epoxycyclohexyl-3,4-epoxycyclohexane carboxylate (CYRACURE UVR-6110) was supplied by Dow Chemical Company. This material is hereinafter referred to as Cyclo. Cyclo has 11.6% oxirane oxygen content. Phosphoric acid (85 wt%), isophthalic acid, benzoic acid, and toluene diisocyanate were laboratory-grade reagents (Sigma-Aldrich).

All other chemicals and reagents used for testing, evaluation, and characterization of oligomers and the cured films were analytical-grade reagents (Sigma-Aldrich). The test panels ($6'' \times 4'' \times 0.032''$) used for the study of film properties were standard low carbon, cold rolled steel (dull matte finish), complying with ASTM A366, supplied by Q-panel Company.

## Synthesis of Oligomers

Four different classes of oligomers were synthesized from the two families of epoxy compounds. The general synthetic procedure used for each class of oligomers are described in what follows. The simplified structural schemes are shown in Figure 3.

### *Synthesis of Phosphate Esters*

For the synthesis of ESO phosphate esters, ESO (150.0 g), and 2-methyl-2-propanol (90–100% based on weight of ESO) were charged into a 500 ml reaction flask under agitation. Phosphoric acid (in varying amounts) dissolved in distilled water (15.0 g) was added to the flask from a dropping funnel at controlled rates of addition (30–45 min) at about 60–70°C. After the addition was complete, the reaction mixture was stirred at 70–80°C for 4 h. The progress of the reaction was monitored by testing samples at regular intervals for percent oxirane content (ASTM D1652–97) and acid number. After the desired acid value (less than 7 mg of KOH) and oxirane contents were obtained, the solvent was distilled off in a rotary vacuum evaporator. The oligomers ESO-Phos-3 and ESO-Phos-5 were prepared by this method using 3 and 5% phosphoric acid by weight of ESO.

Phosphate esters of Cyclo were prepared by the described process but using 2-propanone as solvent in place of 2-methyl-2-propanol. For these oligomers, the phosphoric acid used was 7% (Cyclo-Phos-7) and 10% (Cyclo-Phos-10) based on weight of Cyclo. The characteristics of these oligomers are shown in Table 1. The aforementioned families of phosphate ester oligomers have been characterized by FT-IR spectra to confirm the presence of the functional groups.

### *Synthesis of Alkyl Esters and Polyesters (Benzoates and Isophthalates)*

Oligomers were synthesized from both ESO and Cyclo by their reaction with varying amounts of benzoic acid and isophthalic acid. The general methods for synthesis of ester and polyesters are described in what follows.

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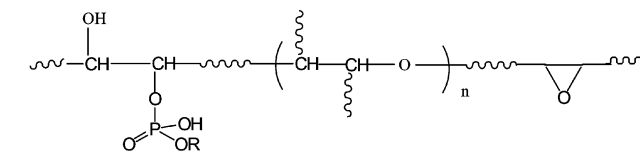
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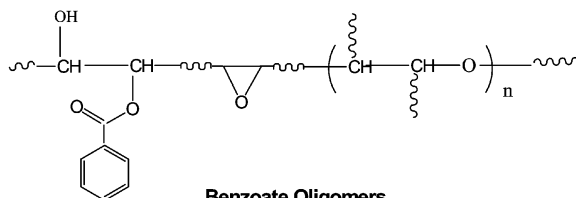
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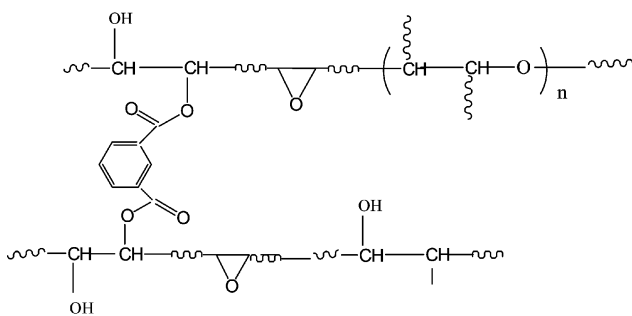
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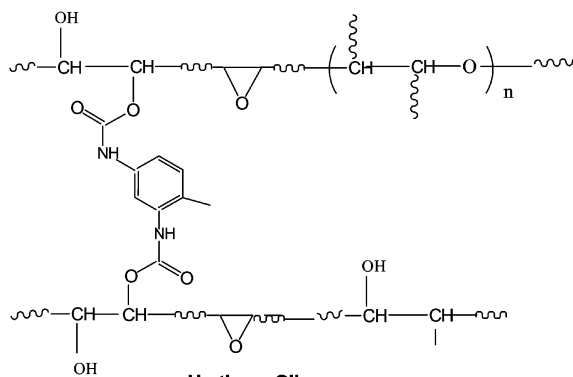
**Urethane Oligomers**

**FIGURE 3** Simplified schematic representations of epoxy functional oligomers.

**TABLE 1** Characteristics of Epoxy Oligomers

| Composition/ identity | Modified by (wt%) | Acid value (mgs of KOH) | % Oxirane O content | Epoxy equi. wt., g | Mole. Wt* g/mole |
|---|---|---|---|---|---|
| ESO derivatives | | | | | |
| ESO | Unmodified ESO | 1.1 | 7 | 228.6 | 930.0 |
| ESO-Phos-3 | Phosphoric acid (3%) | 4.8 | 4.6 | 347.8 | 2801.0 |
| ESO-Phos-5 | Phosphoric acid (5%) | 7 | 3.3 | 484.8 | 2210.0 |
| ESO-BA-7 | Benzoic acid (7%) | 3.8 | 4.6 | 347.8 | 1520.0 |
| ESO-BA- 12 | Benzoic acid (12%) | 6 | 3.2 | 500.0 | 1611.0 |
| ESO-IPA-3 (polyester) | Isophthalic acid (3%) | 5 | 4.6 | 347.8 | 3200.0 |
| ESO-IPA-5 (polyester) | Isophthalic acid (5%) | | Product gelled | | |
| ESO-TDI-3 (PU) | Benzoic acid (7%) & TDI (3%) | 3 | 4.5 | 355.6 | 2315.0 |
| ESO-TDI-5 (PU) | Benzoic acid (7%) & TDI (5%) | 2 | 4.3 | 372.1 | 3625.0 |
| Cyclo derivatives | | | | | |
| Cyclo | Unmodified cyclo | 0 | 11.6 | 137.9 | 252.0 |
| Cyclo-Phos-3 | Phosphoric acid (3%) | 0.8 | 7 | 228.6 | 265.0 |
| Cyclo-Phos-5 | Phosphoric acid (5%) | 1.1 | 5.5 | 290.9 | 285.0 |
| Cyclo-BA-7 | Benzoic acid (7%) | 4 | 6.8 | 235.3 | 452.0 |
| Cyclo-BA- 12 | Benzoic acid (12%) | 5 | 5 | 320.0 | 630.0 |
| Cyclo-IPA-5 (polyester) | Isophthalic acid (5%) | 6 | 5.2 | 307.7 | 2120.0 |
| Cyclo-IPA-8 (polyester) | Isophthalic acid (7%) | | Product gelled | | |
| Cyclo-TDI-3 (PU) | Benzoic acid (5%) & TDI (3%) | 5.3 | 6.9 | 231.9 | 1800.0 |
| Cyclo-TDI-5 (PU) | Benzoic acid 10% & (TDI 5%) | 4.8 | 4.8 | 333.3 | 2018.0 |

*Number average molecular wt. determined by GPC.

Epoxy compound was charged into a reaction flask, mounted on a electrical heating mantle, and attached with a mechanical stirrer, thermometer, and nitrogen inlet. The reaction mixture was heated to about 120°C and a calculated amount of Benzoic acid (or Isophthalic acid) was added in small portions to the reaction flask. After all the

acid was added, the reaction mixture was stirred at 120–130°C, until the acid number was less than 7 mgs of KOH. The reaction mixture was then cooled to ambient temperature. The products were characterized for final acid number and % epoxy oxygen content. The product was thinned, if required, in xylene. The characteristics of these oligomers are reported in Table 1.

### Synthesis of Urethane Oligomers

Oligomers containing urethane groups were synthesized from both ESO and Cyclo, as per the following procedure.

The epoxy compounds were first reacted with calculated quantities of benzoic acid, to generate sufficient hydroxyl groups. Varying amounts of toluene diisocyanate (TDI) were then added at a controlled rate to the reaction mixture maintained at 50–60°C. The reaction was monitored by FT-IR spectroscopic method and the heating was continued until the disappearance of the spectral peak at 2240 cm$^{-1}$. The reaction was catalyzed by the addition of 0.01% of dibutyltin dilaurate, based on the total charge. The characteristics of these oligomers are reported in Table 1.

## Characterization of Oligomers

The oligomers have been characterized by chemical methods for acid value (ASTM D-1639) and oxirane oxygen content (ASTM D-1652). The number average molecular weights have been determined by Gel Permeation Chromatographic technique (GPC), using polystyrene as control. The FT-IR (Nicolet 510P FT-IR spectrometer) was used for monitoring the course of reaction during oligomer synthesis.

## Preparation of Coating Compositions and Cured Films

The cationic thermal cure coating compositions were prepared from the epoxy oligomers by blending 1 wt% (based on vehicle non-volatiles) of ammonium antimony hexafluoride (NACURE Super XC-7231, Ex. King Industries). In order to adjust the viscosity for enabling wet film application, a required amount of xylene was used as solvent. Uniform wet films of these coating compositions were sprayed on test panels so as to get the Dry Film Thickness (DFT) of all the samples approximately 1.0 ml. The test panels, after a solvent flash-off time of 20 min, were placed in an air-oven for 15 min at 100°C. The testing and evaluation of the films were carried out at least after 48 h.

## RESULTS AND DISCUSSION

### Synthesis of Oligomers

In the present work, the primary objective was to derive two families of epoxy functional oligomers containing esters and urethane groups from starting compounds having significantly different chemical structures and properties. For this purpose, the two epoxy compounds selected were ESO and Cyclo. As evident from their chemical structure (shown in Figure 2), ESO has a parent triglyceride structure, having three fatty acid chains bearing epoxide groups. Cycloaliphatic diepoxide compound on the other hand, has a cyclic structure with two epoxy groups, which are more reactive (sterically less hindered) than those of ESO. Attempt has also been made to vary the molecular weights of these oligomers; by using mono and difunctional compounds in their modification, to enable the study of the effect of molecular weight on the ultimate film properties of their coatings.

The chemical modification of the parent epoxy compounds has been carried out using phosphoric acid, benzoic acid, isophthalic acid, and toluene isocyanate to derive phosphate esters, polyesters, and urethane containing epoxide oliomers. The schematic representations of the chemical structures of these oligomers are in Figure 3. Table 1 shows the composition and characteristics of these oligomers. It has been observed that more than the theoretical number of epoxy groups are consumed in the direct esterification method. This is attributed to the substantial extent of etherification, as a result of acid catalyzed reaction between epoxy–epoxy and epoxy–hydroxyl groups [8–10]. These reactions are also responsible for oligomerization and thus increasing molecular weights.

With benzoic acid, oligomers having oxirane oxygen contents as low as 3.2% were synthesized, whereas an attempt made to prepare those having lower than 4.6% with isophthalic acid resulted in premature crosslinking, both for ESO and Cyclo systems. This is attributed to the difunctionality of isophthalic acid.

For the synthesis of urethane-containing oligomers, epoxy compounds were first reacted with benzoic acid to generate sufficient hydroxyl groups, which were subsequently reacted with TDI. Dibutyltindilaurate was used to catalyze the reaction between –NCO and –OH. A small amount of phosphoric acid was added upon completion of the urethane reaction to decompose the basic catalyst, which would interfere with the cationic mechanism during the curing of the films.

The results of the molecular weights (GPC; Table 1) indicate that a certain degree of polymerization (or oligomerization) occurs during the

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direct esterification reaction of epoxy compounds. The GPC results also showed products with a broad range of polydispersity (not shown in the Table 1).

## Film Properties

The primary film properties of the coatings based on ESO and Cyclo are presented in Table 2 and Table 3, respectively. All the coatings were cured at 100°C for 30 min.

## Coatings Based on ESO

All the coating compositions based on ESO, when baked at 100°C for 15 min, resulted in solid films indicating "curing" under these conditions. For both phosphate and benzoate type oligomers, it has been found that MEK double rub numbers, which is a measure of crosslink density (XLD) of the film, decreases as the oxirane content is decreased (Figure 4). This is as expected because decreasing oxirane groups would reduce the number of potential crosslinking sites. The higher MEK double rubs for the films based on polyester and

**TABLE 2** Properties of Coatings Based on ESO*

| Composition/ identity | %Oxirane O content | Dry film thickness mils | Pencil hardness | Adhesion cross-cut | MEK 2 × rubs | Impact res. Ibs × inch | |
|---|---|---|---|---|---|---|---|
| | | | | | | D | R |
| ESO phosphates | | | | | | | |
| ESO-Phos-0 | 7 | 0.95 | B | 5B | 200 | 75 | 15 |
| ESO-Phos-3 | 4.6 | 1.0 | 5B | 5B | 75 | 80 | 160 |
| ESO-Phos-5 | 3.3 | 1.0 | <5B | 5B | 20 | 80 | 160 |
| ESO-esters | | | | | | | |
| ESO-BA-0 | 7 | 1.1 | B | 5B | 200 | 75 | 15 |
| ESO-BA-7 | 4.6 | 1 | 2B | 5B | 125 | 80 | 80 |
| ESO-BA-12 | 3.2 | 1.05 | 4B | 5B | 20 | 50 | 160 |
| ESO-polyester | | | | | | | |
| ESO-IPA-3 (polyester) | 4.6 | 1.1 | H | 5B | 135 | 120 | 90 |
| ESO-PU | | | | | | | |
| ESO-TDI-3 (PU) | 4.5 | 1.05 | H | 5B | 130 | 90 | 60 |
| ESO-TDI-5 (PU) | 4.3 | 1.1 | 2H | 5B | 145 | 135 | 110 |

*Cured at 100°C for 15 min.

**TABLE 3** Properties of Coatings Based on Cyclo*

| Composition/ identity | %Oxirane O content | Dry film thickness mils | Pencil hardness | Adhesion cross-cut | MEK 2 × rubs | Impact res. lbs × inch | |
|---|---|---|---|---|---|---|---|
| | | | | | | D | R |
| Cyclo-phosphates | | | | | | | |
| Cyclo-Phos-0 | 11.6 | 1.1 | 8H | 4B | 200 | 25 | <5 |
| Cyclo-Phos-3 | 7 | 1.0 | 8H | 5B | 200 | 40 | <5 |
| Cyclo-Phos-5 | 5.5 | 1.0 | 8H | 5B | 200 | 60 | <5 |
| Cyclo-esters | | | | | | | |
| Cyclo-BA-0 | 11.6 | 1.1 | 8H | 4B | 200 | 25 | <5 |
| Cyclo-BA-7 | 6.8 | 1.1 | 8H | 5B | 200 | 50 | <5 |
| Cyclo-BA-12 | 5 | 1.1 | 6H | 5B | 175 | 50 | 15 |
| Cyclo-polyester | | | | | | | |
| Cyclo-IPA-5 (polyester) | 5.2 | 0.95 | 6H | 5B | 200 | 110 | 55 |
| Cyclo-PU | | | | | | | |
| Cyclo-TDI-3 (PU) | 6.9 | 1.05 | 8H | 5B | 200 | 60 | 30 |
| Cyclo-TDI-5 (PU) | 4.8 | 1.05 | 6H | 5B | 200 | 80 | 40 |

*Cured at 100°C for 15 min.
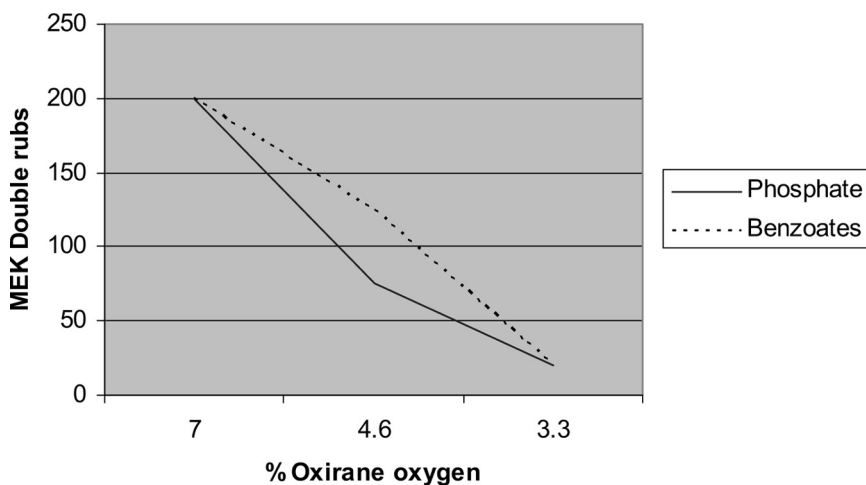


**FIGURE 4** Effect of oxirane content on MEK double rubs for ESO-based oligomers.

polyurethane oligomers (ESO-IPA-3, ESO-TDI-3, ESO-TDI-5), as compared to the phosphates and benzoates having comparable oxirane content, might be due to the higher molecular weight of the former, which produces a more complex matrix of the film through chain entanglement [10].

The pencil hardness values for the films based on phosphates and benzoate oligomers are very low, which can be attributed to the "soft" structure of oil coupled with low molecular weights. Films of Benzoate esters are harder than phosphate esters of comparable oxirane contents. The presence of rigid aromatic structure might be responsible for this effect. Further, it has been found that for both phosphates and benzoates, film hardness improves as oxirane content of the oligomer is increased. Film hardness of both polyester and polyurethane oligomers are substantially superior to the benzoates and phosphates of comparable oxirane content, probably due to the higher molecular weight and chemical structure.

Although there is no significant difference in the impact resistance of the films based on phosphates and benzoates, the films of polyesters and polyurethane are found to have improved toughness. This can be, again, attributed to their higher molecular weight and chemical structure. Adhesion of all the films to steel substrate was found to be excellent.

## Coatings Based on Cyclo

The baked film properties of coatings based on Cyclo are reported in Table 3. In general, all coatings show very high MEK double rubs, high pencil hardness, and poor impact resistance. This can be attributed to the higher (compared to ESO counterparts) oxirane content and the rigid chemical structure of Cyclo. In case of benzoates- and phosphates-based coatings, the effect of reduction of oxirane content (and hence the crosslink density of the film) is not reflected in the film properties, probably because the crosslink densities of these coatings are well above the critical value at which such a change can be noticeable. However, coatings based on polyesters and polyurethanes show improved toughness compared to the phosphates and benzoates having comparable oxirane contents.

## CONCLUSION

A variety of epoxy-functional oligomers can be created by chemical modification of multifunctional oxirane compounds. It is possible to employ these oligomers as self-crosslinking principal film formers in

cationic thermal-cured coatings. Among other factors, the primary film properties of such coatings are significantly dependent on the chemical structure and oxirane functionality of the oligomers. It is possible to design oligomers, by controlling their chemistry and functionality, for their use in specific end-use coatings applications.

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