<u>**Task ID**</u>:   425.031

<u>**Task Title**</u>:   Supercritical Carbon Dioxide Compatible Additives: Design, Synthesis, and Application of an Environmentally Friendly Development Process to Next Generation Lithography: Resists and Additives

<u>**Deliverable Title**</u>:

* Report on the simulation of a series of quaternary ammonium salts for resist development in scCO(2) and their mechanisms of dissolution.

* Report on simulation of additives including silazanes.

<u>**Summary/Abstract**</u>:

Supercritical carbon dioxide ($scCO_2$) has been considered as an environmentally benign replacement for organic solvents in many microelectronic applications. Its unique properties have led to its consideration as a developing solvent for photoresist patterning. However, most conventional photoresists are generally insoluble in $scCO_2$. In this report, a series of quaternary ammonium salts has been synthesized to assist in the dissolution of photoresists in $scCO_2$. The results have established the potential of PBOCST and PHS-co-PS-co-PtBA to be used as negative-tone photoresists in $scCO_2$.

<u>**Introduction**</u>

Carbon dioxide is relatively nontoxic, nonflammable, inert under most conditions and is a potential candidate as an environmentally benign replacement for organic solvents in many microelectronic applications [1]. Supercritical carbon dioxide ($scCO_2$) exhibits unique properties in that it combines liquid-like densities with gas-like diffusivities and zero surface tension. These unique properties have led researchers to consider $scCO_2$ as a developing solvent for photoresist patterning. However, conventional photoresists are often insoluble in $scCO_2$, thereby limiting its practical use. For pure $scCO_2$ processing, several fluorinated or silicon containing polymers have been used as photoresists. Ober et al. have showed the ability to develop custom polymeric materials in $scCO_2$ using otherwise conventional photoresists through inclusion of fluorinated moieties to impart $scCO_2$ solubility[2,3]. It is believed that the presence of fluorine increases the solubility of polymers in $scCO_2$; unfortunately, high fluorine content has an adverse effect on etch resistance. To circumvent such problems, researchers have also explored the use of additives or co-solvents for development in $scCO_2$[4].

Recently, Wagner et al. at Micell Integrated Systems reported the use of CO_2-compatible salts to develop polar polymers in $scCO_2$ [5]. They showed negative-tone development in $scCO_2$ of EUV and DUV photoresists that are normally positive-tone under aqueous development. Their approach has shown good contrast and dense L/S features with aspect ratios>12[6], and has motivated us to study $scCO_2$-compatible quaternary ammonium salts.

<u>**Results and Discussion**</u>

  Experimental Work:

A series of quaternary ammonium salts (QAS) has been synthesized and tested on the development of conventional photoresists in $scCO_2$. The conventional photoresists used were Poly(4-*t*-butoxycarbonyloxystyrene) (PBOCST), Poly(hydroxystyrene-co-styrene-co-*t*-butylacrylate)(PHS-co-PS-co-PtBA), and Poly(methyladamantane-metha-

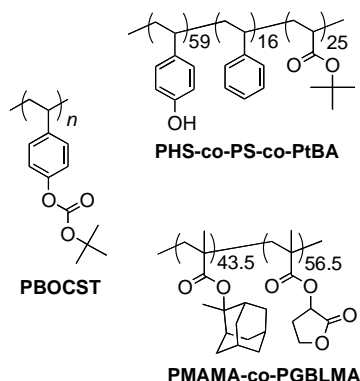crylate-co-α-methacryloxy-γ-butyrolactone) (PMAMA-co-PGBLMA), as shown in Figure 1.

PHS-co-PS-co-PtBA

PBOCST

PMAMA-co-PGBLMA

Figure 1 Chemical structures of conventional photoresists

Synthesis of Quaternary Ammonium Salts

A series of QAS, as shown in Figure 2, was synthesized to be used as a scCO2 compatible additive to dissolve conventional photoresists in scCO$_2$, with the synthetic scheme shown in Scheme 1.
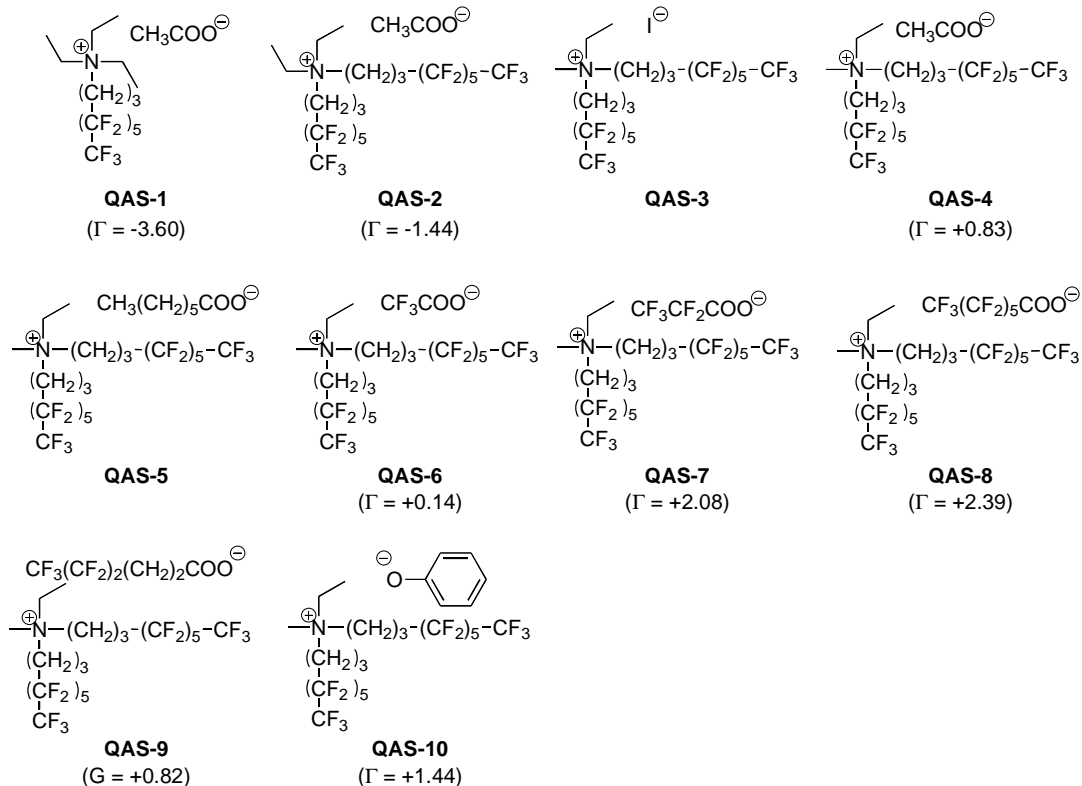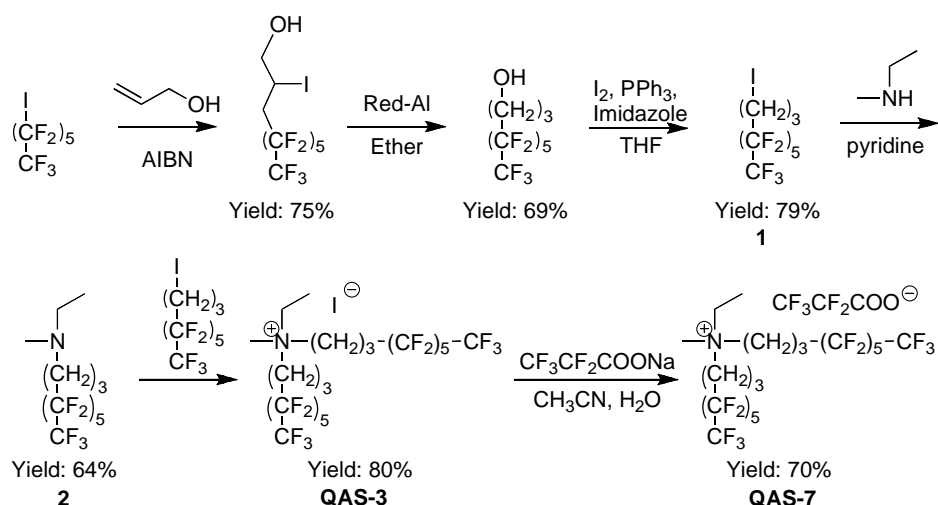

QAS-1
(Γ = -3.60)

QAS-2
(Γ = -1.44)

QAS-3

QAS-4
(Γ = +0.83)

QAS-5

QAS-6
(Γ = +0.14)

QAS-7
(Γ = +2.08)

QAS-8
(Γ = +2.39)

QAS-9
(G = +0.82)

QAS-10
(Γ = +1.44)

Figure 2 A series of quaternary ammonium salts

Scheme 1 Synthetic procedure of QAS-4

The rationale behind the design is that the additive should interact favorably with either the unexposed or exposed photoreisists so that it becomes soluble in $scCO_2$. The ammonium cation center has a high affinity for the polar moieties of the photoresists, and the fluoroalkyl chain imparts solubility to the salt itself in $scCO_2$. The basic nature of the counter anion also plays an important role in controlling the solubility of the salt.

Solubility of a series of QAS in $scCO_2$ was examined at various temperatures and pressures. It was shown that most of the QAS were highly soluble in $scCO_2$ under moderate conditions, especially QAS-4 and QAS-7.

Solubility Test of Conventional Photoresists in $scCO_2$ with QAS

All the conventional photoresists used were insoluble in $scCO_2$ before and after exposure without the additives. The QAS was put into the preheating vessel to help dissolve the polymer films in $scCO_2$, and the polymer films were monitored using laser interferometry. It was shown that PBOCST and PHS-co-PS-co-PtBA with QAS-4 were dissolved in $scCO_2$, and the dissolution rates of PBOCST and PHS-co-PS-co-PtBA in 1.25mM QAS-4/$scCO_2$ solution at $50^{o}C$ and 5000 psi were ca. 40 and 25 nm/min, respectively. However, PMAMA-co-PGBLMA did not show solubility in the QAS-4/$scCO_2$ solution. On the other hand, QAS-7 did not assist in the dissolution of PBOCST, PHS-co-PS-co-PtBA or PMAMA-co-GBLMA in $scCO_2$. Other QAS/photoresists systems have also been examined: QAS-6, QAS-8, QAS-9, and QAS-10 assist in dissolving PBOCST in $scCO_2$, but no effect were shown for PHS-co-PS-co-PtBA and PMAMA-co-PGBLMA.

The exposed (deprotected) photoresists were also developed in the QAS/$scCO_2$ solutions. It was shown that PHS-co-PS-coPtBA became insoluble in the QAS-4/$scCO_2$ solution after exposure at doses of 0.71 to 14.2 mJ/cm^2. The deprotected PBOCST also showed slow dissolution at 1-4 nm/min, which was much slower than the unexposed PBOCST. These results indicate that PBOCST and PHS-co-PS-co-PtBA are potential negative-tone photoresists in $scCO_2$. On the other hand, PMAMA-co-PGBLMA did not

show any solubility in 1.25 mM QAS-4/scCO$_2$ solution at 50°C and 5000 psi after processing for 30 minutes. The solubility results are shown in Table 1.

Table 1 Solubility results of the photoresists

QAS	Polymer	Protected	Deprotected	Note
CH$_3$COO$^{\ominus}$ N$^{\oplus}$—(CH$_2$)$_3$—(CF$_2$)$_5$—CF$_3$ (CH$_2$)$_3$ (CF$_2$)$_5$ CF$_3$ **QAS-4** (1.25 mM)	PBOCST	Dissolution (40 nm/min)	Slow dissolution (1-4 nm/min)	*Negative tone photoresist*
	PHS-co-PS-co-PtBA	Dissolution (25 nm/min)	No dissolution	*Negative tone photoresist*
	PMAMA-co-PGBLMA	No dissolution	No dissolution	
CF$_3$CF$_2$COO$^{\ominus}$ N$^{\oplus}$—(CH$_2$)$_3$—(CF$_2$)$_5$—CF$_3$ (CH$_2$)$_3$ (CF$_2$)$_5$ CF$_3$ **QAS-7** (1.25 mM)	PBOCST	No dissolution	No dissolution	
	PHS-co-PS-co-PtBA	No dissolution	No dissolution	
	PMAMA-co-PGBLMA	No dissolution	No dissolution	

scCO$_2$ Development of an E-beam Patterned Commerical Photoresist

A commercial photoresist donated by TOK was used to evaluate the lithographic performance. The protected TOK photoresists showed a constant dissolution rate of 15nm/min in scCO$_2$ with either QAS-4 or QAS-7. On the other hand, the deprotected TOK photoresist showed a slow dissolution rate of 1 nm/min. The contrast curves of the TOK photoresist developed in both QAS-4/scCO$_2$ and 0.26 N tetramethylammonium hydroxide solutions are shown in Figure 3. The dissolution test of the TOK photoresist in the QAS-7/scCO$_2$ has also revealed a negative tone behavior.
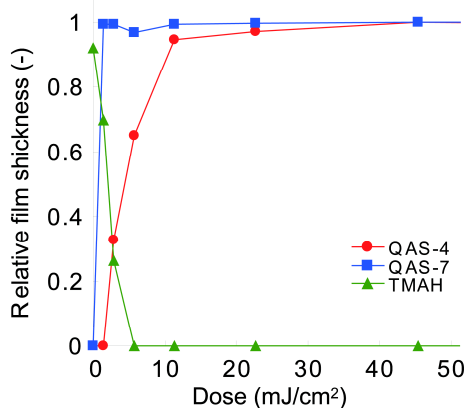

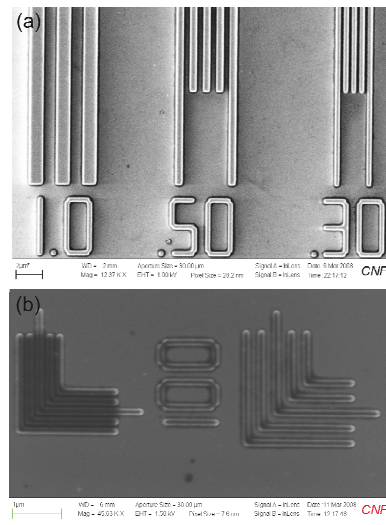**Figure 3** Contrast curves of TOK photoresist

Figure 4 (a)SEM image of TOK photoresist patterned by e-beam lithography with an exposure dose of 107 µC/cm^2 and developed in the 1.25mM QAS-4/scCO$_2$ solution for 60 min at 50°C and 5000 psi (b) in QAS-7/scCO$_2$

The results of e-beam patterned TOK photoresists developed in the QAS/scCO$_2$ solutions are shown in Figure 4.

Proposed Mechanism

The interactions between the QAS and the photoresists depend on the ion pair energy, the shape and size of the mobility of the ions. We have found good solubility of protected PBOCST in scCO$_2$ in the presence of the QAS because the electro-negative oxygen atom in the carbonate group can easily interact with the electro-positive ammonium center to provide a CO$_2$-friendly environment, which allows the salt to pull the polymer into scCO$_2$. It is found that as the polymer chains dissolved into scCO$_2$ from the film, each chain formed its own spherical globule with the *tert*-butyl tails of each monomer creating a non-polar outer shell. The QAS molecules bind to the surface of the polymer file, but have limited interactions with the dissolved species. These micelles do not form freely in the absence of QAS, which indicates the micelle stabilization by the QAS. For the deprotected PBOCST, removing the t-BOC group increases polymer-polymer dipole interactions by the resulting hydroxyl groups, which lowers the interaction with the QAS and decreases its solubility in scCO$_2$.

The oxygen atoms in the hydroxyl group and carbonyl group of the unexposed PHS-co-PS-co-PtBA can undergo electrostatic interaction with the ammonium cations. The reason that PHS-co-PS-co-PtBA did not dissolve in QAS-7/scCO$_2$ in contrast to QAS-4/scCO$_2$ was due to the ion pair energy of the salt, which depends on the basic nature of the anion. The fluoroalkyl carboxylate anion in QAS-7 is less basic than the carboxylate anion in QAS-4 because of the inductive effect of the fluorine substitution. There was a weaker interaction between QAS-7 and the polymer, so it is unable to shield the hydroxyl group of PHS-co-PS-co-PtBA and the polymer was still insoluble in scCO$_2$. For the deprotected PHS-co-PS-co-PtBA, removing the *tert*-butyl group made it more polar and thus did not dissolve in scCO$_2$.

Computational Simulations:

In order to rationalize or interpret our experimental observations, and with the goal of arriving at design principles that can be used to guide the synthesis of new, more effective additives for dissolution in CO2, we have undertaken a comprehensive molecular modeling approach that includes quantum mechanical and statistical mechanical calculations of realistic molecules and the various aspects of the dissolution process in scCO2. The computational results of our work to date are summarized in the table below. Green denotes success, red failure, and yellow is potential pass. A system in which only one form (exposed or unexposed) was tested is a potential pass. White squares are untested by simulation either because the given additive was not intended for that photoresist (as is the case for QAS11-14 with ESCAP or PHOST) or experimental results were available before simulation that already proved the system unworkable (PHOST with QAS7). Specific systems are discussed in more detail below.

Photoresist	QAS4	QAS6	QAS7	QAS11	QAS12	QAS13	QAS14	Isocyanate	TMDS	HMDS	none
Additive											
ESCAP	🟩	🟩	🟥					🟨	🟨	🟨	🟥
193nm				🟥	🟥	🟥	🟩	🟩	🟩	🟩	🟥
PHOST	🟩							🟨	🟩	🟩	🟥
Molecular Glass	🟥	🟨	🟩								🟨

Summary of computational results. Green denotes success, red failure, and yellow is potential success.

Since photoresist chemistries are proprietary, we used three model resists; ESCAP, 193, and PHOST as mentioned above (Figure 1). ESCAP and PHOST are EUV resists and 193 is a 193nm photoresist.

For the computation component of this collaboration, model parameters were used from the Optimized Potential for Liquid Simulation (OPLS) force field. Additional quantum calculations were performed to provide a more accurate charge model, necessary to accurate describe ionic species and aromatic ring interactions. Using this model, thin films of resists were equilibrated in the presence of $scCO_2$. Free energy curves were produced by integrating the average force on each chain as a function of position throughout the film. Systems with lower free energy at the surface of the film are thermodynamically unstable and will be soluble, whereas those with lower free energy at the center are insoluble.

Our work with additives has focused primarily on the use of quaternary-ammonium salts (QAS). It was previously demonstrated[5] that using QAS additives with $scCO_2$ can allow for the development of 42nm lines with at 12:1 aspect ratio and no pattern collapse. As we discovered through computational molecular modeling, QAS are effective additives due to the ability to have a polymer-favoring ion (anions for the species we considered) and a $scCO_2$-favorring ion (cation). We expanded upon the previous research by testing14 different QAS formulations, by experimental and computational means. Depending upon QAS, it may disassociate during use, but is otherwise unreactive.

We found QAS4 (structure below) to be the most effective additive QAS for ESCAP resist and QAS14 to be the most promising for the 193nm resist. This effectiveness of QAS4 with ESCAP was found by experiment. Simulation of that system revealed clustering of resist hydroxyl groups around the anion provided a mechanism by which to hide polar regions of the photoresist, making it soluble in $scCO_2$.

QAS4 structure
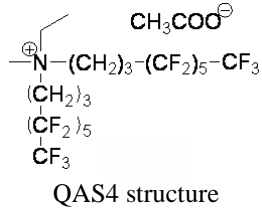
QAS14 was found by simulation to be the only QAS capable of solubilizing the 193nm resist. Experiments have yet to confirm this result. Here simulation is ahead of experiment.


QAS14 structure
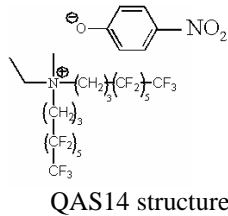
Based upon the success of QAS4 with our model resist, a commercial formulation was obtained from TOK which was expected to be similar to ESCAP. Using a solvent of $scCO_2$ + QAS4, we were successfully able to produce the features shown in figure 4.

We also examined the use of some reactive additives, most notably an isocyanated-based structure shown in the figure below (referred to as isocyanate). From a modeling perspective, handling reactive additives requires first examining the unreacted species to determine the appropriate dissolution mechanism. For species that react more quickly than the unreacted species penetrates the polymer film, a fully reacted surface layer will form, whose relative solubility will control dissolution. For a species that reacts slowly, there will be a mechanism of bulk penetration and reaction. For our systems, the former is the most accurate model.

Chemical Formula: $C_{11}H_4F_{17}NO$
Molecular Weight: 489.13
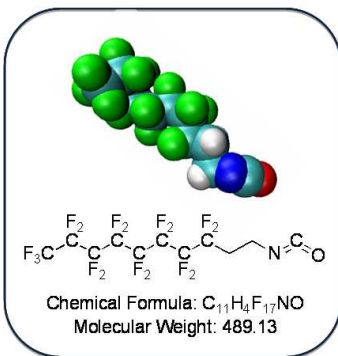
Based on our examination of isocyanate with our resists, it was found to be highly effective at developing photoresist. This was confirmed by both experiment and simulation.
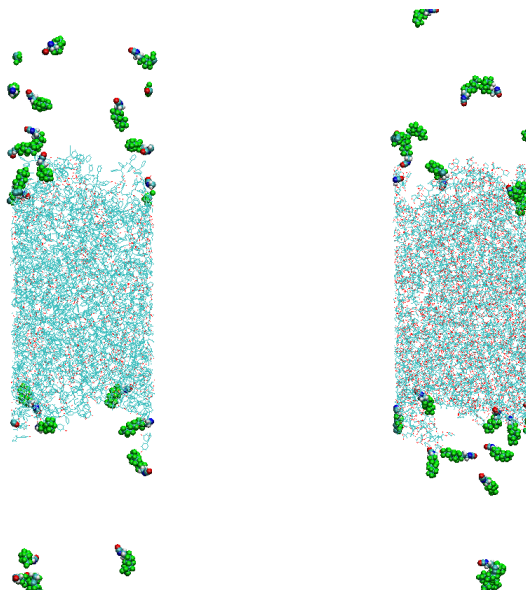
Unreacted isocyanate additive (predominately green spheres) in the presence of polymer film (cyan, red, and white lines) with scCO$_2$ hidden for clarity. System on the left is ESCAP, and system on the right is 193nm-resist. In both cases the unreacted additive does not penetrate significantly into the film, indicating that a surface reaction mechanism is most probable.

The other class of system with have examined with scCO$_2$ are molecular glass photoresists. Molecular glasses have inherently low LER, making them ideal photoresists. Via simulation we were able to rapidly screen this new resist with our library of QAS to find an optimal choice, QAS7. Unfortunately, after this material was later synthesized, it was found to be a liquid at process conditions, and a search for a different molecular glass formulation is currently under way.
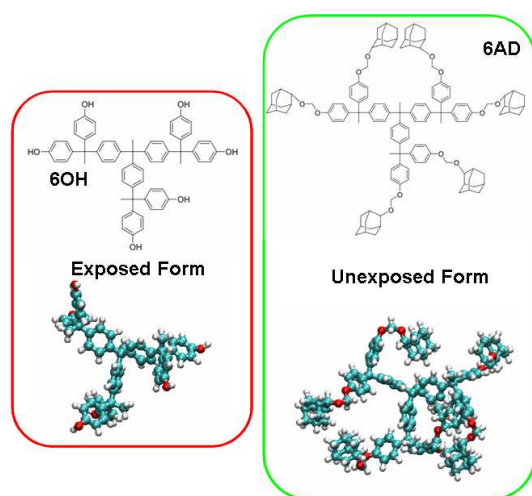
All in all, we have examined a large number of systems over the last two years and demonstrated the potential of scCO$_2$ to be used as a lithographic solvent.

3.Future Work

In order to make the process more environmentally benign, the possibility to design non-fluorinated additives has also been considered. Beckman [8] has reported that

the interactions between oxygen-containing functional groups and CO_2 such as acetate groups are important for designing non-fluorinated CO_2-soluble molecules. Previously, Kazarian et al. [9] has also reported the existence of Lewis acid-base interactions between CO_2 and the oxygen of a carbonyl. Structures of potential additives we plan to use are shown in Figure 5, where the acetate groups are considered to be capable of interacting with both the photoresists and $scCO_2$. The solubility of photoresists in $scCO_2$ with the aid of these non-fluorinated molecules will be tested. In addition, the relationship between the numbers of acetate groups on the additives and $scCO_2$-solubility will also be investigated.
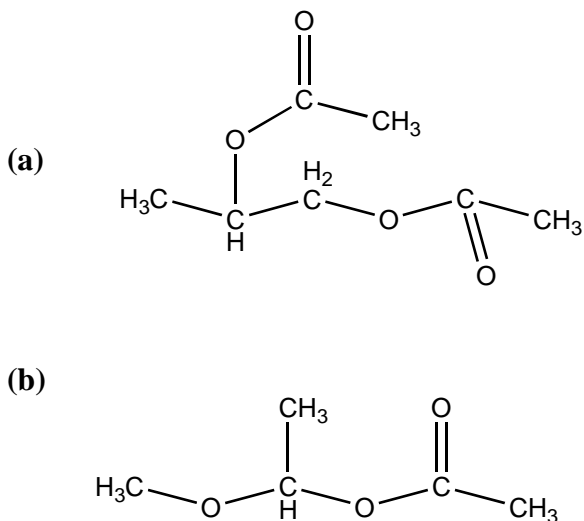
(a)

(b)

Figure 5 Chemical Structures of Potential Non-fluorinated Additives

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