The use of fluoropolymers for non-stick cooking utensils

P. Thomas
DuPont, R & D Laboratory, A. Spinostraat 6, 2800 Mechelen, Belgium

History

It was in the spring of 1938 that Dr R Plunkett, working at DuPont's Jackson laboratory in New Jersey, discovered PTFE. During the Second World War the polymer was used for strategic military applications.

In 1946, DuPont started to commercialize granular PTFE under the well known trade name TEFLOn®.

In 1951 the first coating based on a mixture of chromic/phosphoric acid with a PTFE aqueous dispersion was marketed mainly for industrial applications where non-stick and/or dry lubrication was required. When applying such a coating on a metal substrate, roughened (eg by grit blasting) and stoving at 430°C, the acids react with the metal and form mixed chromium/phosphorus oxides providing excellent adhesion to the substrate. They act also as a hard matrix to impart abrasion resistance to the coating. This coating is still used today.

The author believes that it was also in 1951 in the USA that the first application of a non-stick coating on a frying pan was achieved. Two applicators licensed by DuPont coated a number of frying pans as Christmas gifts for friends and employees with the chromic/phosphoric acids and PTFE mixture as described above.

Between 1951 and 1960, the primer/topcoat, two-coat system was developed. This system is based on a pigmented PTFE dispersion topcoat applied on the single chromic/acid coat formulated earlier which then becomes a primer. At this time, the coatings were used mainly for the food processing industries such as bakeries and sweet factories.

In 1956, the French engineer Marc Gregoire founded the well known French cooking utensils company TEFAL®, (the contraction of TEFLoN® and Aluminium), which was the first in Europe to coat frying pans. An acid etched aluminium disc was coated with PTFE dispersion applied in several layers. The coating was stoved and pressed in the etched surface to provide adhesion. The disc was then formed into a frying pan.

Because PTFE is not melt processable, and in order to reduce the melt viscosity and crystallinity of the polymer, DuPont launched FEP in 1960 (a copolymer of tetrafluoroethylene and hexafluoropropylene) which could be extruded like other thermoplastics. FEP had been used in coatings for mold release by 1961 and is still in use for industrial food applications (industrial bakeries, small bakeries, confectionery). The advantage of FEP over PTFE is its good melt flow characteristics and lower crystallinity which yield low coating porosity particularly suitable in hot humid conditions like bakeries.

It was also in 1961 that the U.S. FDA (Federal Food and Drug Administration) accepted the use of non-stick coatings for cooking utensils. Sales became significant from 1964 in the USA and from 1970 in Europe thanks to the intense advertising and public recognition of the exceptional non-stick/easy-cleaning properties of the coating.

Over the years coating technology with fluoropolymers improved considerably, especially regarding adhesion and abrasion properties. The principles of obtaining adhesion to substrates and the phenomenon of stratification of fluoropolymers have been reviewed by K. Battar. The paper presented here deals more particularly with the use of PTFE copolymers in the formulation of non-stick coatings for cooking utensils.

The only copolymers which are of interest in this review are FEP and PFA because of their superior thermal stability and their compliance with the health requirements of such as FDA and BGA (BundesGesundheitAmtes - Germany).

FEP became commercially available due to the availability of HFP (Hexafluoropropylene) monomer. Even poly-HFP could be synthesized at ultra high pressure but today about 10 weight % HFP co-monomer is incorporated in the polymer backbone. Although FEP is melt processable, it has a lower thermal stability than PTFE. Therefore research was conducted to find another melt processable fluoropolymer which would have a heat resistance closer to that of PTFE.

It is the synthesis of HFPO (Hexafluoropropylenoxide) that opened the route to several other perfluorinated polymers including PFA,5 which became commercially available in 1973. HFPO can be converted to PPVE the co-monomer of TFE to manufacture PFA. About 5 weight % of PPVE is used in the copolymer to obtain a true thermoplastic (PFA) which has excellent chemical resistance and heat stability, very similar to those of PTFE.

In 1985 a three coat material for non-stick cooking utensils was launched commercially with PTFE/PFA dispersion blends in order to reinforce the abrasion resistance of the coating. It was found that the higher degree of toughness of PFA compared with that of PTFE was an advantage to improve the abrasion resistance of the coating.

The use of FEP in cooking utensils coatings is more recent (1991). An outstanding property of FEP, when added to the constituents of primers, is the promotion of the adhesion of the coating to the metal substrate. This allows the adhesion of very low surface tension fluoropolymer coatings to substrates having extraordinary low surface roughness. The benefits of both FEP and PFA copolymers in cooking utensils application will be reviewed in detail.

Coating technology for cooking utensils

In this section a short review will be given of the most important principles of coating technology applied to non-stick cooking utensils.
Formulation

The techniques used for formulating a non-stick coating have been borrowed from standard practice in paint technology. Like most of the paint formulations, it comprises four main components:

- the polymer(s)
- the pigment(s)
- the solvent(s)
- the additive(s)

A requirement of the pigments used in non-stick cooking utensils is good thermal stability. Most of the organic dyes are not suitable because they decompose at the processing temperature of the coating. The solvents have an important role in controlling the viscosity during the application as well as in the formation of the film. The additives have various important functions (e.g., stabilizing dispersions) but are added generally below 5% weight on the total formulation. The major component of the formulation is the polymer.

Various polymers can be present in a non-stick formulation but they can be divided into two categories:

- fluoropolymers
- binders

The binders are usually present in primers where they play an essential role in promoting the adhesion of the coating. A list of the structures of the most currently used binders is provided. The structure of the polyamideimide polymer which is probably the most used binder in non-stick cooking utensils formulations is in Figure 1.

The fluoropolymers used in non-stick formulations are essentially:

- PTFE (by far the major fluoropolymer present in the coating formulation)
- PFA and FEP (whose concentrations do not exceed approximately 40% of the total fluoropolymer content of the coating)

Generally, these fluoropolymers are used as 52-60% weight solids dispersion in water. In other cases, micropowders (~1 micron particle size) are dispersed in solvent-based formulations, used principally for bakeware or industrial applications.

Stratification

PTFE dispersions have a very high melt viscosity ($10^{11}$-$10^{13}$ Pascal sec) and they do not flow very well at their melt temperature ($527$-$335^\circ$C). To help the flow, the coating is ‘sintered’ at a higher temperature in the range of $400$-$430^\circ$C for a short time (1-5 minutes). At this temperature, the other thermally unstable organic components of the formulation evaporate or decompose (e.g., surfactants, acrylics). During the sintering operation the fluoropolymer stratifies (depending to a various extent on the nature of the fluoropolymer and the quantity in the formulation) to the surface of the coating in order to minimize the surface energy. As PTFE possesses a very low surface tension (19-20 dynes/cm), it separates from the other components, especially from the binder which will concentrate at the metal interface. This phenomenon is called stratification.

The role that FEP and PFA play in the stratification mechanism will be discussed further.

Film structure

Coatings used for non-stick cooking utensils are generally of multiple layer composition. The first layer (called the primer layer) plays an essential role for the adhesion of the coating. The binder is usually only present in the primer layer to promote adhesion. Successive layers of fluoropolymer are applied on the primer to provide the non-stick properties. The total film thickness of the film ensures the durability of the coating (mainly: scratch resistance, release property, gas and liquid permeation).

The adhesion of the primer is very much dependent on:

- the surface preparation (cleanliness, roughness...)
- the ratio of fluoropolymer/binder
- the degree of fluoropolymer stratification

The degree of fluoropolymer stratification is probably the property which is the most difficult to control. However, two key requirements control stratification:

- melt viscosity of the fluoropolymer or fluoropolymer blends
- curing conditions (time and temperature)

Note that curing conditions are not only essential to provide the mechanical properties of the film, they also control the energy provided to the system to allow the stratification phenomenon to take place. An under-cured film will show insufficient abrasion resistance and poor adhesion.

Finally, a minimum amount of fluoropolymer is required in the primer to promote intercoat adhesion with the top layers.

A microscopic picture of a cross section of a typical coating for non-stick frying pans is shown in Picture 1.