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The Use of Toner-Toner Charge Spectra to Generate a Pigment Triboelectric Series

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Abstract

A triboelectric series orders a set of materials by the sign of the charge of each material when one is rubbed against the other. This can be done for toners by placing two toners of interest in a small vial, mixing them vigorously, and then sampling the mixture in a charge spectrograph. Almost invariably the toners charge against one another, and some separation is observed in the charge spectra. If the toners differ only in pigment, the relative charge of the toners should indicate the relative charge of the pigments. This has been done for a set of typical pigments melt blended into a polyester resin. Mixing all possible combinations of two toners leads to a self consistent ordering of the pigments. When the process is repeated after a silica surface additive has been blended onto the individual toners, a self consistent triboelectric series can again be generated; however, the ordering is different from that generated from the unblended toners. Ordering the toners by the charge level generated when each is mixed with a polymethylmethacrylate coated carrier generates yet another ordering of the pigments. Possible reasons for the variation in triboelectric ordering will be discussed.

Introduction

Each of the color toners used in a xerographic copier or printer is based on a unique pigment or blend of pigments, and these in turn affect many of the properties of the toner beyond color alone. In particular it is known that different pigments typically generate different levels of charge on their associated toners when prepared in similar formulations and mixed with the same carrier formulation. For example, Macholdt and Sieber have made toners incorporating pigments in styrene-methacrylate copolymers and charged them against carrier coated with the same polymer.[1] They showed that the blowoff tribos of the resultant developers covered a wide range of values.

One can also talk about arranging pigments in a triboelectric series. The definition of a triboelectric series is that any substance higher in the series will charge positive relative to those lower in the series. One can directly generate a triboelectric series for pigments in toner by mixing two toners with different pigments and then looking for charge separation in the mixture. The charge separation can be detected in a device such as the charge spectrograph. In the instrument used at Xerox a sample is injected into a uniformly flowing column of air while it is simultaneously subjected to a perpendicular electric field. When the sample is collected on a porous sheet at the bottom of the column the displacement of each toner particle from the zero axis is proportional to its individual charge to diameter ratio. If the sample consists of a mixture of two colors that are distinguishable by the eye, one can easily determine which of the two is more positive.

The charge spectrograph used here is a design proprietary to Xerox, but commercial instruments are available from Hosokawa Micron and Epping.[3,4] The instrument from Hosokawa Micron, called the E-Spart Analyzer, analyzes particles in a flowing stream by size and mass and may not be suitable for distinguishing particles by color. On the other hand the Epping device collects the particles on a substrate and could probably be used for experiments similar to those described here.

Experimental

Each of the following pigments was blended with a polyester resin in a Banbury mixer at a 2% weight loading (Table 1). The toners were prepared primarily to look at color properties, and the loading was low to avoid pigment saturation effects. This did not affect our ability to detect charging differences in the pigments.

Table 1. Pigments used in Study

Common Name	Pigment
Green	Pigment Green 7
Orange	Pigment Orange 13
Purple	Pigment Violet 1
Reflex Blue	Pigment Blue 61:1
Rubine Red	Pigment Red 57:1
Violet	Pigment Violet 23
Warm Red	Pigment Red 53:1
Yellow	Pigment Yellow 14

For simplicity we will drop the use of the word "Pigment" in future references and also denote the toner by the corresponding pigment; thus Orange 13 denotes the toner made with Pigment Orange 13.

The Banbury blends were jetted to a 7 micron volume weighted average size, but the resultant toners where not classified to remove large and small particles.

To test the relative triboelectric nature of two pigments, a tenth of a gram of each of the two corresponding toners was placed in a 1 ml plastic vial and shaken vigorously for 15 sec using a Wig-L-Bug shaker.[5] The mixture in the vial is then sampled by dipping a wooden or metal probe into the toner. This typically leaves a thin layer of toner on the sampling tool, and this layer is blown into the charge spectrograph with a gentle jet of air. The composition of the vial and the sampling spatula was varied and found to have little effect on the resulting charge distributions. The length of time on the Wig-L-Bug does affect the charge distribution, with longer times leading to narrower distributions, but does not affect the relative positive or negative nature of the charging.

With a dispersion field of 200 V/cm the resultant traces were typically anywhere from 2 to 20 mm wide centered at the zero point of the charge spectrograph with clearly distinct colors on the positive and negative tails of the distribution. The pigment corresponding to the color on the positive side is placed above the pigment on the negative side in the triboelectric series. All possible combinations of two toners where examined, and a single ordering of the pigments was found to satisfy all the data. The triboelectric series generated is thus self consistent. This series is given in the No Additive column in Table 2.

Table 2. Triboelectric Series from Toner-Toner Spectra

	No Additive	1% Silica
Most Positive	Red 53:1	Red 53:1
	Red 57:1	Red 57:1
	Violet 23	Violet 1
	Blue 61:1	Blue 61:1
	Yellow 14	Violet 23
	Orange 13	Yellow 14
	Green 7	Green 7
Most Negative	Violet 1	Orange 13

Note that the triboelectric series can be generated without reference to the width of the charge distribution or the degree of separation of the colors. It is only referring to which is the more positive color. In any triboelectic series the degree of separation of two materials is not a quantitative predictor of the amount of charge generated when they are contacted; it only predicts which of the two is positive. In the present case the width of the total distribution is not strictly a function of the degree of separation of the pigments in the tribo series. However, there was a clear trend in the degree of separation when a single toner was compared against a set of toners arranged in their triboelectric series.

The same set of eight toners was ball mill blended with 1% of a 7 nm fumed silica for 30 minutes. The toner-toner mixing experiment was then repeated with the new set of toners. Again, it is possible to construct a self consistent triboelectric series from the data, but it is not completely consistent with the series generated for the toners without the surface additive (Table 2). Red 57:1 and Red 53:1 continue to be the most positive toners, but many others have shifted places.

Each of the toners, both with and without surface additive, was blended with a polymethylmethacrylate (PMMA) coated steel carrier at a toner concentration of 4% and roll milled for 15 minutes. The developers were then characterized both by their blowoff tribo (charge to mass ratio, Q/M) and by the charge spectrograph (charge to diameter ratio, Q/D). In the following table the toners are ordered by Q/D with the most positive Q/D regarded as equivalent to the most positive in the triboelectric series. Q/D is used since the unclassified character of the toners may introduce variability to Q/M. Also, Q/D showed a larger percentage spread than Q/M, increasing a factor of 2.7 from low to high for the No Additive case versus 2.0 for Q/M, and increasing a factor of 1.5 versus 1.2 for the Additive case.

Table 3. Two Component Charge without Additives

Pigment	Q/M	Q/D
Red 57:1	-20	-0.24
Violet 1	-22	-0.29
Blue 61:1	-31	-0.33
Yellow 14	-35	-0.47
Green 7	-36	-0.48
Violet 23	-39	-0.52
Red 53:1	-39	-0.63
Orange 13	-39	-0.64

Table 4. Two Component Charge with Additives

Pigment	Q/M	Q/D
Violet 1	-43	-0.43
Blue 61:1	-42	-0.46
Red 57:1	-42	-0.49
Yellow 14	-45	-0.57
Violet 23	-49	-0.58
Red 53:1	-53	-0.58
Orange 13	-54	-0.63
Green 7	-53	-0.64

There is actually little disagreement in ordering by either Q/M or Q/D. Only in the additive case are there two instances of disagreement, and these only involve a single tribo unit. The range of values in the additive case is significantly smaller than the no additive, and the values are generally higher. This is to be expected, since the silica acts as a negative charge control agent.[6] Its character will tend to dominate, raising overall charge levels and reducing the effect of the pigments. This also means that the ordering in Table 4 is least likely to reflect the intrinsic triboelectric character of the pigments, even as it is the case most resembling the use of pigments in contemporary xerography.

Discussion

If we put all our tribo series in one table, we find that we have four distinct series (Table 5). As before the pigments on the top are the most positive and the pigments on the bottom are the most negative.

Table 5. Triboelectric Series

Ton-Ton No Add	Ton-Ton 1% Silica	Two Comp No Add	Two Comp 1% Silica
Red 53:1	Red 53:1	Red 57:1	Violet 1
Red 57:1	Red 57:1	Violet 1	Blue 61:1
Violet 23	Violet 1	Blue 61:1	Red 57:1
Blue 61:1	Blue 61:1	Yellow 14	Yellow 14
Yellow 14	Violet 23	Green 7	Violet 23
Orange 13	Yellow 14	Violet 23	Red 53:1
Green 7	Green 7	Red 53:1	Orange 13
Violet 1	Orange 13	Orange 13	Green 7

The "Toner-Toner No Additive" case is that which most closely matches the definition of a triboelectric series, although even here we have introduced the toner resin. The resin may combine in different ways with the individual pigments so that the triboelectric character of the blend is not the same as the pigments themselves. Thus we are really determining the triboelectric series for a set of pigments in polyester resin.

Raw pigment could be mixed in the vials and blown into the charge spectrograph to obtain a pure pigment-pigment tribo series. However, the spectrograph is designed and optimized to work with toner sized particles rather than the much smaller pigment grains. Also, there is concern about staining the spectrograph with pigment that cannot be easily removed. As a result, all the work has been done with toner.

The "Toner-Toner 1% Silica" case adds another layer of complexity by introducing a surface additive. This could be distributed differently on the different colors depending on the triboelectric interaction between the silica and the pigment. Since silica is quite electronegative, it can be expected to interact most strongly with the most positive pigments and perhaps cover them more readily than more negative pigments. Thus we are now comparing the relative triboelectric character of two particles with different pigments which are in turn covered more or less with a silica that can substantially alter the triboelectric character of the particle.

Another possibility is that the pigment may have a dye component. By this we imply that it can have a component that is molecularly dispersible and hence not fixed in its original toner matrix. This component may stain not only the silica during the initial blending of silica and base toner but also the silica toner blend of the other pigment during the Wig-L-Bug mixing. This will alter the triboelectric character of all the components and can lead to a change in ordering. Violet 1, the pigment that shows the largest shift, is a laked dye and may be showing this effect.

The "Two Component No Additive" case is the closest to the work of Macholdt and Sieber. However, there is a distinct difference. By coating the carrier with the toner polymer Macholdt and Seiber were essentially comparing the relative charging ability of the pigments (in the polymer matrix) against the toner polymer. By using a different polymer on the carrier the present work compares the relative charging ability of the combined pigment-polyester matrix against polymethylmethacrylate. Macholdt and Seiber are closer to isolating information about the pigments themselves, but they are not directly comparing the triboelectric character of the pigments. The use of a second polymer for the carrier coating does compare the relative charging of the pigments in a manner closer to how they are actually used.

The "Two Component 1% Silica" case comes closest to evaluating the pigments as they are actually used in xerographic applications but also involves all the possible interactions discussed above between pigment, toner polymer, silica, and carrier polymer. In the end it may determine the utility of the pigments, but it may bear little relation to the relative intrinsic charging of the pigments.

Conclusion

There are many ways of comparing the triboelectric character of different pigments. Each can give a different ordering of the pigments. The ordering given by a well defined triboelectric series based on the relative charging of pigment against pigment in toner may be lost by the time pigments are blended into toner, the toner is mixed with surface additives, and the blends are mixed with carrier to form a developer.

References

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Biography

Dr. Paul Julien is a Principal Scientist for The Document Company, Xerox, in Webster, New York, responsible for designing toners and developers for new marking technologies. Working at Xerox since receiving his Ph.D. in Physics in 1977, Dr. Julien has been associated with toner design and evaluation for over 20 years. In that time he has earned over 20 U.S. Patents and has contributed chapters to four books related to toner technology.