

## Communication Between Corporate Analytical and Manufacturing: A Polymer Problem.

A polyimide (PI) is made by reacting an aromatic dianhydride (DAN) with an aromatic diamino ether (DA).



This is a process for a new polymer which has novel and useful properties. The polymer was commercialized eight months ago, and is very successful. The process, however, suffers from several problems, including variability in the quality of the monomers, particularly the DA.

The DA process included a crystallization from an alcohol solvent using a decolorizing carbon. Last month, the supplier of the carbon decolorizing agent went out of business, and an alternate source was found. Polymer made since the changeover has not had consistently acceptable properties.

The problem was presented to you via a written memo from the technical director of the DA plant. She asked you to find the impurity in the new, ineffective decolorizing carbon. A sample of the offending carbon and a retained sample of the previous supply was attached.

You are mass spectroscopist who has been with the company for 3 years. Your familiarity with polymer production is minimal. The memo was directed to you because the Technical Director read an article in ChemTech a few months ago discussing the great power of newer mass spectrometry techniques.

What is your response to the memo?

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The telephone as an analytical tool: call the Technical Director and ask for more background concerning the nature of the problem.

The director tells you that the production facility has been shut down, 200 staff members are furloughed, and the future of a new profitable business is in jeopardy.

Assume your technician had a three week backlog of samples to run, and you were already working 10 hours/day. Discuss the level of importance you should apply to this request.

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You are assured that the only change has been the source of the carbon, and analyze the impurities in the carbon. Extraction of all organic material and mass spec analysis demonstrates no differences between the carbons.

Does this analysis demonstrate that the carbons are identical?

The Technical Director of the polymerization plant has been informed by the staff of the DA plant that the DA they are making frequently fails a color test. (In a standardized procedure, the transmission in solution of the DA made since the change in carbon source is as much as 6% off that of a pure white standard. Any more than a 1% deviation results in the failure of a "polymerization test" run at the polymer plant.

The polymerization facility is 200 miles from the location of the monomer plant.

The polymerization test used by both plants is a controlled lab polymerization which is considered successful if a goal viscosity is reached under the test conditions without the formation of gel. The Technical Director tells you that the color test is a reliable predictor of polymerization success.

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You call the DA plant, speak to a chemical engineer who oversees the process, and request samples of "white" and defective DA.

You separate the colored component from the 'bad' DA by chromatography and determine by IR that it is N,N-dimethyl paraphenylene diamine.

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A discussion with a polymer chemist down the hall convinces you that there is no obvious route by which the color former can lead to gel formation in the polymerization test. It, however, can cause chain termination. The concentration of this contaminant proved unrelated to the polymerization test.

Further work demonstrates a second impurity in all samples of DA. Mass spectrometry identifies it as a trifunctional derivative of DA. . No pure C24 was available for calibration, but an IR absorption band was ratioed against an internal band to form a specification for usable DA. However, there is a poor correlation between the trifunctional impurity and the color of the sample.

You convince the DA plant to run the polymerization test with controlled amounts of the dimer in spite of the lack of a correlation with color. They demonstrate that this trifunctional material results in failure of the polymerization test.

The problem seems not to be related to the color as had been assumed for years.

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Small amounts of trifunctional impurity, C24, such as are found in the satisfactory DA, do not interfere with the polymerization.

You call the Technical Director at the polymer plant and inform her that if the C24 level is kept low, the polymerization test would be passed.

She points out that her question wasn't really " what was causing the failure of the test" but "how do we ensure consistent output from the plant."

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You return to a review of the chemistry. Dimer formation clearly depends on some critical reaction parameter which changes when the new source of carbon is used. You suspect a catalytic effect, re-investigate the carbon. No differences were found in the types of inorganic impurities. It had already been shown that there were no differences in extractable organic impurities. It was eventually determined that the original carbon was unusually basic. You do not do a mechanistic study, but assume that the basicity suppresses C24 formation.

Working with the DA plant you work out conditions for modifying the carbon and making DA which passes the polymerization test.

Knowledge that the new carbon was not itself introducing deleterious materials allowed other process changes to duplicate the original polymerization conditions. The polymerization test could be consistently passed using DA made under the new conditions provided C24 was maintained below a certain limit.

You proudly write a 15 page description of the entire 'detective story', giving the plant the details of your thinking and describing the theory of the analytical methods. Your memo leads up in an orderly fashion to your conclusions.

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### A Problem Again

Your relationship to the plant is aggravated when you are informed the next day that the DA plant finds your answer incorrect. They have run the polymerization test with DA that has less than the critical amount of C24 monomer, and it still failed. The technical director tells you they intend to bring in an outside consultant, rather than trusting to Analytical.

The consistent results fell apart even worse when attempted by the polymerization plant (a few hundred miles away). The client (polymerization plant) reasonably wanted the monomers to pass it successfully before a plant run was made.



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The polymerization lab immediately informed analytical that they had solved nothing because the DA make under the new conditions still failed the lab test. It must be remembered that the test had been developed by the client's lab, and the plant had depended on it for several years.

The test had proven not to be robust when Analytical was applying it, and they suspected that it had some deficiencies. Rather than discuss the problem directly with the client, Analytical reviewed all aspects of the polymerization test.

The solvent used was dry dimethylacetamide (DMAC). The known sensitivity of polymerization reactions to trace moisture led to analysis of the water content of the solvent. The DMAC was dried over molecular sieve that was efficient but slow in removing trace moisture. (Operators, to save time, were cutting back on the contact time with the drying agent.) However, good reproducibility could be obtained at a specified water level. The conclusion was that excess water would mitigate the cross linking effect of the trifunctional C24. Holding the water constant made the C24 the only variable in the 'end use' test.

With this knowledge Analytical could explain to the client what was causing the problem. The client then had only to correlate the result of the 'end use' polymerization test with the actual plant polymerization conditions, and to determine the C24 limits which could be tolerated.

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It is now 5 years later, and the new polymer is proving to be a big seller. The monomer plant is too small to satisfy the demand and an external source of monomer is found. The second company that manufactures the monomer also has a limited capacity. As the polymer finds more uses, your company increases its order from the outside supplier. The first shipment at the larger quantity results in the same problem the plant had experienced years ago.

Long discussions with the supplier bring out the fact that to meet the demand, the supplier raised the temperature of a drying process to increase productivity.

Successful processing turns out to require that the water level in the solvent be precisely on specification, neither above or below.