Identification of High Performance, Low Environmental Impact Materials and Processes Using Systematic Substitution (SyS)

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INTRODUCTION

Process analysis can identify opportunities for efficiency improvement including cost reduction, increased safety, improved quality, and decreased environmental impact. A thorough, systematic approach to materials and process selection is valuable in any analysis. New operations and facilities design offer the best opportunities for proactive cost reduction and environmental improvement, but existing operations and facilities can also benefit greatly. Materials and processes that have been used for many years may be sources of excessive resource use, waste generation, pollution, and cost burden that should be replaced. Operational and purchasing personnel may not recognize some materials and processes as problems. Reasons for materials or process replacement may include quality and efficiency improvements, excessive resource use and waste generation, materials and operational costs, safety (flammability or toxicity), pollution prevention, compatibility with new processes or materials, and new or anticipated regulations.

Very often, material and process substitution is performed in a nonsystematic manner. While a material or process may be identified as a problem, often the substitution decision is made “on the fly.” Personnel may rely on vendor recommendations and specify substitute materials and processes without a systematic analysis of alternatives. Such decisions may lead to sub-optimal performance, increased waste generation, higher life cycle costs, and increased risks. The authors cannot stress too greatly the need for a thorough, systematic evaluation of an operation’s materials and processes with the goal of decreased cost, waste, and pollution. If replacements are to be made, it is logical to identify the best possible replacements systematically to minimize life cycle cost, risk, and the need for future replacements or modifications. The so-called “rule of ten” applies to this situation. That is, if a change made at the design stage costs $1, that change at prototype stage costs $10, and the change at operational stage $100.

Many factors must be considered in most materials and process substitutions. The number of alternatives and their different characteristics can be overwhelming if a methodical system of evaluation is not used. Additionally, it is uncommon that one or two personnel will be able to understand all the implications of alternatives’ characteristics. There should be involvement from team members with good knowledge of the material or process use, materials properties, engineering, health and safety, operations management, and waste management. Involvement of these personnel also helps ensure acceptance of the new material or process.

The net result of a systematic evaluation, as described below, is a small set of top-ranking alternatives to evaluate in the laboratory and, after further downselection, prototype or pilot testing. Candidates should be tested against the current material or process before final selection is made, to eliminate alternatives that have unanticipated disadvantages, and to identify the best option from those with similar evaluation scores. Again in the evaluation phase, personnel from a number of disciplines, including the operations personnel, should be involved to obtain the widest possible input on the advantages and disadvantages of the selections. Once sufficient testing is completed, the team makes the final choice.

Properly evaluating substitute materials and processes should be part of a larger process for achieving high quality and environmental excellence. Quality and environmental management tools include process mapping; life cycle cost analysis; an effective employee involvement program; identification of opportunities for improvement; action plan development and implementation, including use of evaluation methods such as SyS; quantitation of results, management by fact; and a continuous improvement program. Achievement of quality and environmental excellence, and associated goals such as energy efficiency are being recognized through state and federal programs such as Energy Star, Climate Protection, and New Mexico's Green Zia. Such recognition motivates organizations to additional achievement and is good publicity, but more importantly the programs instituted result in improved efficiency and cost savings.

DESCRIPTION

The authors have developed a systematic substitution (SyS) process applicable to a wide variety of materials and processes. SyS incorporates a refinement of a technique reported previously (Nimitz a). While SyS is certainly not unique, and the weighted ranking matrix for scoring candidates has been used for many years, we have found the overall SyS process highly effective in identifying high performance substitutes without being overly complex and costly.

The logical, methodical SyS process identifies and ranks candidate materials and processes for given applications. The process has been used successfully in several projects for a variety of applications (Kuchar, et al.; Nimitz b-g, Shell, et al., Toohey, et al.). The steps of the SyS process have been given in a previous paper (Nimitz h) but are listed here in somewhat more detail and for completeness.

(1) <u>Determine all requirements</u>, including performance; compatibility; stability; regulations; cost sensitivity; safety (toxicity and flammability); and maximum allowable environmental impact. Establish the advantages and disadvantages of the current material or process versus the requirements. The extremes of the requirements define the limits of acceptable properties for a candidate replacement. Team members (e.g., floor personnel, production engineers, ES&H, waste management, and operations management) should be included in this process for their valuable input and "buy-in" to ensure acceptance of the ultimate results.

(2) <u>Develop a list of evaluation criteria</u> based on the requirements. In SyS, criteria are often grouped under the main headings of physical properties, performance, toxicity, compatibility, environmental effects, and cost, all of which may be further subdivided as desired. There are obviously some differences between evaluating a process versus a material. For a process,

the toxicity heading may have grouped under it the toxicities of all the materials involved in the process. Performance criteria may include estimated energy efficiency, throughput, product quality, ease of use, and any existing test data for similar applications. Physical data may include (for process equipment) dimensions and weight, and (for materials) molecular weight, density, strength, ductility, wear resistance, vapor pressure, viscosity, heat capacity, thermal stability, electrical resistivity, etc. Compatibility and other chemical data for materials may include flammability and compatibility with metals, plastics and elastomers, and other chemicals. Environmental criteria for materials may include factors such as atmospheric lifetime, ozone-depletion potential (ODP), global warming potential (GWP), total equivalent warming impact (TEWI), volatile organic compounds (VOCs), regulatory status, waste disposal, and air and aquatic toxicity of materials and wastes. Environmental criteria for processes may include materials criteria plus waste generation, resource use (including utilities), emissions, and potential severity of accidental spills and releases. Toxicity criteria for materials may include exposure limits, carcinogenicity, teratogenicity, odor, and sensitization.

(3) Develop an initial list of candidates for consideration. Sources for candidate materials may include chemical databases (e.g., Chemical Abstracts Service, Beilstein, Gmelin), relevant literature, and vendor information. Sources for candidate processes may include personnel knowledge; scientific and technical journals; vendor literature; U.S. and international patents; government laboratories and publications; and information on competitors and benchmark organizations. If possible, include known competitors' and benchmark organizations' current materials or processes for comparison.

(4) Assign relative weights to evaluation criteria on a scale of one to ten points based on which are judged more important and more accurately known. Other factors being equal, higher uncertainty means lower confidence in data values and assignment of a lower relative weight. This step can be one of the most involved parts of the SyS process. The working team must reach consensus on the weightings before the evaluation process proceeds, and this consensus should be documented. If the weightings are later found not to reflect the true requirements for some unanticipated reason, they can be changed by consensus, although such changes should be made only when necessary.

(5) Collect and tabulate properties of reference materials or processes, and the candidate replacements. Reference materials or processes include the material or process to be replaced and corresponding materials or processes used by competitors or benchmark organizations. Estimate unreported properties as needed, and assign realistic uncertainties to the estimations. Estimation of unreported properties involves some uncertainty. The actual properties could be better or worse than estimated. Using the worst possible value may eliminate a good candidate. Using the estimate may overestimate the value of the property. It has been our experience that at this stage it is better to keep a marginal candidate than to eliminate a good candidate, so the estimate is typically used as is. The uncertainty should be listed with the value.

(6) If reasonably accurate numerical values are available for the data, develop a point scale of 0-10 for data values for each criterion, where 0 is least attractive and 10 is most attractive, and

assign scores for each candidate for each criterion. If numerical values are not appropriate or not available, assign subjective descriptions to the value of each criterion for each candidate (e.g., very high, high, moderately high, moderate, moderately low, low, or very low), then assign numerical values to the subjective descriptions (e.g., very high = 10, high = 8 etc.). First-time SyS users should probably use a linear mapping of points to criteria values. However, in this step experienced SyS users can add a certain amount of sophistication. The mapping of numerical values to the point scale need not be linear. As an example, assume a substitute cleaning solvent is being sought. For the substitute cleaning solvent the allowable viscosity range is 0.5 to 5.5 centiPoise (cP). On a linear scale, a solvent with a viscosity of 2 cP will get a 7 score and a solvent with a viscosity of 3 cP will get a 5. However, because low viscosity is valued for both good penetration and effective draining, the solvent with a viscosity of 2 cP should get a proportionately higher score because low viscosity is important for two reasons. The scoring function can be a polynomial function, an exponential function, some other type of function, or even values chosen manually. In this example, the function should result in a value of 0 at 5.5 and a value of 10 at 0.5, and it should have higher values than a linear mapping when viscosity is low. What function is used to map point scores depends on the relative importance of individual values within the allowable value range. This is different from the weightings assigned in Step 4 above. The weightings reflect the importance of the criteria against each other. Score mapping curves are used to adjust the scores of values within a criterion. Score mapping is an intracriterial process.

(7) Sum the products of the criteria weights times the individual scores for each candidate to give weighted rankings. Any spreadsheet program can be used for this step. Table 1 shows the type of table used for property tabulation and scoring.

(8) Evaluate several of the highest-ranking candidates in the laboratory and at pilot scale, then test the highest-ranked candidate in the facility.

Table 1. Sample Table for Property Tabulation and Scoring

Category	**Evaluation Parameters**	**Weight**	**Candidate 1 data**	**Candidate 1 score**	**Candidate 2 data**	**Candidate 2 score**
Physical	Freezing point					
	Liquid density					
	Molecular Weight					
	Viscosity					
	Etc.					
Performance	(vary with application)					
Compatibility	With metals					
	With polymers					
Toxicity	Acute inhalation					
	Ames					
	Chromosomal damage					
	Etc.					
Environmental	Atmospheric lifetime					
	GWP					
	ODP					
	Partition coefficient					
	Etc.					
Weighted total score						

RESULTS AND DISCUSSION

The SyS process has identified good substitute materials and processes in a variety of applications. Several examples are discussed below.

Space Shuttle Heat Transfer Fluid

The hydrochlorofluorocarbon (HCFC)-21 is used as a heat transfer fluid in the Space Shuttle. However, HCFC-21 is a Class 2 ozone-depleting substance whose production has been halted under the Montreal Protocol and HCFC-21 has relatively high toxicity with a Threshold Limit Value (TLV) of 10 ppmv in air. Its high toxicity complicates Space Shuttle maintenance operations. An environmentally friendly, nonflammable, low toxicity, inexpensive heat transfer fluid for potential use in the Space Shuttle and other applications was desired. Ideally, the replacement should be a drop in or near-drop in replacement for HCFC-21.

Working with NASA and contractor personnel, ETEC identified the requirements for the replacement fluid, screened over 100 candidates, downselected to the best ten candidates, and finally selected the three best candidates. NASA and contractor personnel eliminated one of the three best candidates because, although it was not flammable and would have saved significant launch weight, it was combustible at high temperature. The heat transfer rates of the two remaining candidates, HFC-245fa and HFE-7100, were calculated for the Space Shuttle system and HFC-245fa was identified as the best candidate. HFC-245fa was estimated to transfer heat about 8 % better than HCFC-21 under typical Space Shuttle cooling loop conditions. HFC-245fa is considerably less toxic than HCFC-21. Although exposure limits have not yet been officially set, HFC-245fa is expected to have a Permissible Exposure Limit (PEL) of 500 to 1000 ppmv in air. HFC-245fa is compatible with all Space Shuttle cooling loop materials, and it would save about 8 kg launch weight versus HCFC-21. HFC-245fa will also soon be in bulk production by Honeywell (formerly AlliedSignal) as a replacement for HCFC blowing agents in the manufacture of rigid, closed cell polymer insulating foams, and its cost is expected to be $8 - $10 per kilogram.

Following identification of HFC-245fa as the top candidate, ETEC evaluated its heat transfer rate versus HCFC-21 at bench scale in a circulating heat transfer loop with tubing size, linear flow rate, pressurization, and warm and cold side temperatures matched to the Space Shuttle cooling loop conditions. Multiple runs were made with HCFC-21 and HFC-245fa. Relative standard deviations were 1.2% or less, and the results showed a heat transfer rate for HFC-245fa that was 12 - 13% greater than HCFC-21's heat transfer rate.

Cleaning

In a project for the U.S. Air Force, ETEC worked with BDM Federal, Inc. to review use of a large vapor degreaser used to clean aluminum honeycomb for aircraft wing repair. The vapor degreaser used 1,1,1-trichloroethane (TCA). Because TCA is being phased out under the Montreal Protocol as a Category 2 ozone-depleting substance, a new cleaning method was desired. The new method had to be environmentally friendly, use a nonflammable, low toxicity cleaning agent, leave no corrosive residues, and clean aluminum honeycomb adequately to give a surface that would bond strongly with epoxy. A review and evaluation of possible cleaning methods (nonaqueous, semi-aqueous, and aqueous) showed the attractiveness of aqueous cleaning. Approximately 50 aqueous cleaners were evaluated. Note that in this project there were two phases to the evaluation, the evaluation of types of cleaning (i.e., nonaqueous, semi-aqueous, and aqueous) then the evaluation of cleaners (50 aqueous cleaners). This project involved evaluation of both a process and a material, and such evaluations can often be logically divided in this manner. The top three aqueous cleaner candidates were evaluated in the laboratory. Laboratory evaluation involved tests of cleaning abilities, adequate penetration of the honeycomb, corrosion during cleaning, corrosive residues as revealed by accelerated aging, and compatibility with nondestructive crack-detection methods (no residues left in cracks to interfere with dye penetrant). An aqueous spray cleaning system was identified as the most attractive alternative to vapor degreasing for aluminum aircraft honeycomb. This custom system was designed and built, and is now in place at the National Defense Center for Environmental Excellence (NDCEE).

In a project for the U.S. Air Force Research Laboratory, a new group of nonaqueous, nonflammable, low atmospheric impact solvents was evaluated for aircraft maintenance critical cleaning operations. The solvents were perfluoro-n-propyl iodide (1-C_3F_7I), perfluoro-n-butyl iodide (1-C_4F_9I), and perfluoro-n-hexyl iodide (1-$C_6F_{13}I$) and their blends with conventional solvents. Evaluation of physical properties, stability, compatibility, toxicity, and cleaning abilities identified perfluoro-n-butyl iodide, given the trade name Ikon® Solvent P, as the top-ranking iodofluorocarbon (IFC) solvent. Perfluoro-n-butyl iodide has physical properties and cleaning abilities very similar to CFC-113, and is superior to CFC-113 for removing perfluorinated greases. Its rat 4-hr LC_{50} of 14,000 ppmv is considerably higher than that of 1,1,2-trichloroethane (2,000 ppmv) and approximately the same as 1,1,1-trichloroethane and trichloroethylene (18,400 and 12,500 ppmv, respectively). Perfluoro-n-butyl iodide is Ames-negative and is not clastogenic by the human lymphocyte test. Because IFCs photolyze quickly in sunlight to simple, natural products, perfluoro-n-butyl iodide has an atmospheric lifetime of only about 2 days, giving it essentially zero (<0.0025) ozone-depletion potential (ODP) and an extremely low global warming potential (GWP) of less than 2 (relative to CO_2 = 1) for a 100 year horizon. NASA Kennedy Space Center (KSC) sponsored an additional effort to determine perfluoro-n-butyl iodide's potential suitability as a cleaner for oxygen systems. The new solvent was found to be quite compatible with oxygen and an excellent candidate for oxygen system cleaning, particularly as it is even more effective than CFC-113 at removing fluorinated greases. The project sponsored by the Air Force Research Laboratory also investigated thirty-six conventional flammable solvents to blend with IFCs. The conventional flammable solvents were also evaluated using SyS, and were scored on physical properties, flammability, thermal stability, estimated fractionation from the IFCs, environmental impact, toxicity, and cost. The result of the SyS evaluation was a list of 19 high ranked potential blends. When these potential blends were evaluated in the laboratory two nonflammable near-azeotropes were discovered, one of which was practical as a solvent blend. The blend has been given the trade name Ikon® Solvent M. Ikon® Solvent M's cleaning effectiveness is not quite as good as Ikon® Solvent P for some soils, but it is less expensive and will have a higher exposure limit.

Thrust Vector Control Fluid

The Minuteman Stage II rocket was designed to use Halon 2402 (1,2-dibromotetrafluoroethane) as a liquid injection thrust vector control (LITVC) fluid. This fluid is injected into the exhaust stream, where it decomposes to form a large volume of gas that deflects the exhaust stream to steer the missile. Because of the phaseout of production of Halon 2402 as a Category 1 ozone-depleting substance under the Montreal Protocol, a replacement had to be found. It was most desirable that the replacement use the existing hardware to avoid expensive redesign and testing. ETEC worked with GenCorp AeroJet to identify the required properties, examine an initial list of over 1000 candidate replacements, model performance, downselect the candidates, and choose the most attractive candidate for performance testing. The material selected was perfluorohexane, which has excellent stability and compatibility, low toxicity, and acceptable performance. Although in some applications perfluorocarbons are released to the atmosphere and cause concern about global warming, in this application they undergo combustion and are not released to the atmosphere.

Refrigerants

In a project for NASA KSC, SyS was used to identify top-ranking components for new high performance, nonflammable, zero ODP, stable, compatible, azeotropic or near-azeotropic refrigerant blends to replace ozone-depleting chlorofluorocarbon (CFC) and HCFC refrigerants phased out or facing phaseout under the Montreal Protocol. Ozone-depleting refrigerants that could be replaced include R-12, R-22, R-500, R-502, and R-123. R-12's production has already been phased out in developed countries, R-22's phaseout will start in 2003, and R-123 will shortly follow R-22. R-500 is a blend that contains R-12 and R-152a. R-502 is a blend that contains R-22 and R-115. Available substitutes such as R-134a, R-404A, and R-410A do not have as high innate energy efficiency and performance as desired.

Approximately 100 possible refrigerant components were screened and ranked. Fractionation and performance of potential blends were modeled using ETEC's proprietary AZEO and COOLS computer programs and the National Institutes of Standards and Technology (NIST)'s Refprop® refrigerant properties database. From the screening a set of attractive candidate components were selected. The candidate components were then blended, tested for flammability and performance, and developed into Ikon® Refrigerants A, B, and C. These refrigerants have attractive physical properties, zero ODPs, and low total equivalent warming impacts (TEWIs). They appear suitable to replace R-12, R-22, R-500, R-502, R-123, R-134a, R-404A, R-407C, and R-410A in residential refrigerators, residential and commercial air conditioners, commercial and industrial water chillers, commercial and industrial refrigeration, industrial process coolers, and other cooling and refrigeration equipment that has relatively low leak rates. From all data known so far, the three refrigerants appear superior in performance and environmental properties to any other available alternatives.

Performance tests on Ikon® A and Ikon® B in a 1.75 ton water chiller test bed at ETEC, a compressor calorimeter at Oak Ridge National Laboratories, a 20 ton air conditioning unit at NASA Kennedy Space Center, and a residential refrigerator have shown that both have 10-15% higher energy efficiency and 10-15% greater volumetric cooling capacity than R-12 and R-134a. Ikon® A and Ikon® B also have a total of over five years run time in several refrigerated transports ("reefers") at Dole Fresh Fruit with no indications of incompatibility. Both Ikon® A and Ikon® B have been approved under the U.S. Environmental Protection Agency's Significant New Alternatives Policy (SNAP) program as ozone-depleting refrigerant replacements in multiple applications including residential refrigerators, air conditioning, refrigerated display cases, and water chillers. Initial performance tests on Ikon® C in ETEC's 1.75 ton water chiller test bed show that it has about 95% of the capacity of R-22, and 4-5% higher energy efficiency than R-404A, R-407C, or R-410A. Ikon® C has a low evaporator temperature glide and operating pressures almost identical to R-22. Ikon® C may be usable as a direct replacement in R-22 equipment with an oil change, and can definitely be used as a replacement with a compressor change. A SNAP application has been prepared for Ikon® C.

Firefighting

In a project for the U.S. Air Force, trifluoromethyl iodide (CF_3I) was identified as an effective replacement for Halon 1301 for fire suppression in unoccupied areas. Subsequent testing showed excellent performance and environmental properties, and this chemical was approved as a halon replacement for use in unoccupied areas under the SNAP program. CF_3I is being installed in a variety of facilities in Australia and the Far East, and has recently been named the preferred choice as a substitute fire suppression agent for the F-16 fuel tanks.

CONCLUSIONS

A systematic approach to materials and process substitution is valuable for product quality improvement, process efficiency improvement, cost reduction, increased safety, waste and resource use reduction, and pollution prevention. The SyS process has proven successful in identifying high performance, energy-efficient, low life cycle cost, safe, and environmentally friendly replacement materials and processes for both highly specific and more general applications.

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