# Identification, Evaluation and Development of New Products for Environmental Benefit

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Major societal and economic drivers suggest that there will be a continuing need into the next century to develop evolutionary and revolutionary products/processes that are environmentally benign. Achieving this is far from trivial. The historical record shows that new products sometimes can have unintended environmental impacts.

Breakthrough innovations are a requisite for the continued growth and economic health of industry and society. Such innovations will, based on experience, be discontinuous (Rice et al., 1998), replete with stops and starts, redirections, and spin-offs. In the past decade, companies whose growth rests on their ability to effectively and rapidly innovate, have adopted a structured approach to new product development. Thus, many companies currently use some form of the Stage-Gate product development process derived from the model developed by Robert Cooper of McMaster University (1993). The sequence includes the idea stage, the preliminary assessment stage, the product concept stage, development, testing, trial, and launch. Looking at the overall system, remembering the driving force of environmental benefits, and considering all aspects of potential environmental impact will maximize the likelihood of success.

**Table 1. Freon 22 vs. HFCs**

| Product | Formula (Composition) | BP, °C |
|---|---|---|
| R22* or Freon 22 | $CHF_2Cl$ | −41 |
| R134a | $CF_3CFH_2$ | −27[736] |

Consider a few important new product development examples. The first example is refrigerants which have taken us from direct contact issues ($SO_2$) to replacement with CFCs [once considered miraculous because they made many everyday conveniences a reality, but potentially related to an almost impossible-to-predict environmental consequence (ozone layer depletion)], and then to the current need for new replacement products in terms of HFCs. The second group of examples, such as products for smog abatement and low volatility organic compounds, clearly meet the environmental need and offer benefits to be factored into new product thinking.

## Refrigerants

In the late 20s, the DuPont Company sold more than half of the refrigerant gases employed in small home and commercial units. The most common refrigerant was sulfur dioxide whose major feature was low cost. In 1929, more than 100 people died in a Cleveland hospital from a presumed leak in the refrigeration system (*New York Times*, May 16, 1929), leading to the demand for a new product.

Thomas Midgley of Cornell University (former GM chief chemist) was commissioned in 1928 to work on new refrigerants for Frigidaire, a GMsubsidiary. Because of its physical properties and low toxicity, dichlorodifluoromethane (Freon 12) soon emerged as the leading candidate. GM asked DuPont to develop a manufacturing process and a DuPont-GM JV, Kinetic Chemicals Co., (Hounshell and Smith, 1988), built a 1.5 ton/d plant which came on stream in December 1930. Thus, the era of Freon based refrigerant systems was born. For a half century, the chlorofluorocarbons industry flourished with refrigerant applications as well as in the construction industry where Freon-based fluids have been employed as "blowing agents" to provide the precious air sacs needed in insulating materials.

An article in *Nature* first discussed the potential relationship of chlorofluorocarbons and the stratospherTic "ozone hole" in 1974 (Rowland and Molina), certainly an unintended impact. The Montreal Protocol of 1987 created a demand for the identification, evaluation and development of new refrigerant fluids and new "blowing agents" to avoid this concern. Compressor engineers, synthetic chemists, and environmental scientists collaborated to create systems that are now in place and meet the regulations implemented under the Montreal Protocol. Not only did the refrigerant fluid have to change, but so did the companion lubricant. With chlorofluorocarbons, typical mineral oils were sufficient to provide critical compressor lubrication. Mineral oils, however, are immiscible with hydrofluorocarbons, and new families of products had to be developed. Thus, newly patented *systems* for refrigeration are in place (Hagihara and Sakai, 1992). The approach taken was to identify fluids with similar heat capacity and compare other properties to those of the chlorofluorocarbons while eliminating the chlorine content believed potentially responsible for impacting stratospheric ozone. Further, these products would have to be produced at costs which ultimately would be borne by the consumer and via production routes which themselves are environmentally benign and do not exacerbate any emissions issues (air, water, or solids). Table 1 shows the boiling points of chlorodifluoromethane (R22) and a hydrofluorocarbon intended to replace Freon 22.

The nomenclature convention is as follows:

$R_{xyz}$ $x$ = no. of carbon atoms –1, $y$ = no. of hydrogen atoms +1,
$z$ = no. of fluorine atoms and unfilled bonds occupied by chlorine

All isomers have the same number designation; letters are used to distinguish isomers according to their symmetry. Thus, for

R134*a*, *a* represents the unsymmetrical distribution of four fluorine atoms across the two carbons. Thus, the preferred refrigerant has moved from sulfur dioxide (potentially toxic) to Freon (suspected of impacting the stratospheric ozone protective layer) to hydrofluorocarbons. The nature of the polarity of hydrofluorocarbons render them immiscible with the mineral-oil-based lubricants employed with chlorofluorocarbons necessitating a new lubricant type. The lubricant search ultimately led to oxygenated organics including polyalkylene glycols (PAGs), esterified PAGs and, importantly, polyol esters such as:

$$C_2H_5\text{–}C(CH_2OCOR)_3$$

where $R$ is $C_4 \rightarrow C_8$ linear or branched.

The refrigerant lubricant product story is still unfolding. A parallel story occurred in the building insulation business where alternative blowing agents have now been introduced (Blanpied and Thornsberry, 1996).

## Products for smog abatement

There are numerous manifestations of this concern culminating in the enactment of regulations intended to improve air quality. Recently, the Clean Air Act Amendments of 1990 mandated the use of cleaner burning hydrocarbon fuels. Beginning in 1992, approximately 40 urban areas in the U.S. were required to use oxygenated fuels during the winter months to help meet ambient carbon monoxide standards. A second provision requires "reformulated gasoline" (RFG) to be used in the nine cities with ozone levels classified as "severe" or "extreme" beginning in 1995. Most gasoline suppliers have been meeting the oxygenate requirements (and getting an octane boost as well) by adding methyl tertiary butyl ether (MtBE) to gasoline blend stocks. MtBE was originally incorporated into gasoline to provide octane when the environmental concerns about tetraethyl lead, resulted in the phase-out of leaded gasoline. MtBE is the oxygenate used in about 85% of RFG, which, in turn, accounts for about one third of all U.S. gasoline sales. Recently, various agencies, most notably the California Environmental Protection Agency, have raised concerns regarding the detection of MtBE in surface and ground water (Chemical Week, 1998), and in March, 1999 Governor Davis of California issued an Executive Order calling for the removal of MtBE in gasoline sold in California by December 31, 2002 (Executive Order, 1999). The challenges facing the refiners now include providing a motor gasoline product for California, which will be free of MtBE, have the necessary oxygen content, deliver the required octane at an acceptable vapor pressure, provide the necessary infrastructure for manufacture and distribution, be a product without a new set of environmental problems, be cost-effective, etc. In addition, the refiners and chemical companies in the MtBE business need to find alternate uses for the MtBE or its components, isobutane and isobutylene and methanol, and hopefully to utilize the equipment currently employed in the manufacture of MtBE.

Another example of the role of technology in environmentally beneficial new product development is the search for products that will enable original equipment manufacturers in the automotive industry to meet their corporate average fuel economy (CAFE) requirements. In order for manufacturers to meet requirements, they can create new systems, create new components for existing systems, or some combination of both. It is understood that the lower the viscosity of an engine oil, the higher the fuel economy. Thus, over time, the viscosity of lubricating oils has gone down. The need remains for an oil film to be preserved at shutdown to minimize metal to metal wear at startup. Additionally, the oil must be resistant to thermal breakdown under high load conditions. And, longer drain intervals are desired. Additives can and do provide many performance features, which in combination with the right base stock provide the needed attributes.

Aset of lubricant specifications is close to approval for the next-generation passenger car motor oils—International Lubricant Standardization and Approval Committee (ILSAC)-GF3. The new specifications are driven by federal mandates for longer emission control system durability, greater fuel economy, the automakers' desire for lower oil volatility (lower emissions), and reduced additive depletion. This combination drives people toward such solutions as molybdenum additives for reduced friction and to stabler synthetic-base stocks including esters for maintenance of viscosity through lower volatility and thus fuel economy retention. Premier oils today (Mobil 1 brand oil, Ultron brand oil, etc.) are full synthetics. Any new product would likely have to deliver improved performance while not requiring a massive reformulation effort. Some intriguing options have recently been published (Schlosberg et al., 1996).

## Low volatile organic compound products

Anyone who has painted a room or furniture knows the difference in texture and performance of oil-based vs. water-based coatings. Oil-based products are generally volatile organic compounds (VOCs). A *Wall St. Journal* article (May 14, 1999) describes efforts in Southern California by the South Coast Air Quality Management District to dramatically reduce the 70 ton/d of VOC released in the area by primers, sealers and other coatings materials. As usual, this is both a challenge and an opportunity. VOCs contribute to ground-level ozone formation through a complex series of photochemical reactions greatly simplified in the schematic below:

$$NO_2 + h\upsilon \rightarrow NO + O(^3P) \tag{1}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M (M \equiv \text{air}) \tag{2}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{3}$$

and

$$CH_4 + 4O_2 \rightarrow H_2O + CH_2O + 2O_3 \tag{4}$$

where $CH_4$ represents the simplest alkane.

A useful definition of the tendency to form ozone that closely relates to VOC is that of incremental reactivity (Carter and Atkinson, 1987), where incremental reactivity = g ozone formed per g of VOC added to a VOC mixture representative of conditions of urban and rural areas in a given air mass. Ethane with an incremental reactivity of 0.024 was chosen as the standard, and only those organics whose incremental reactivity is ≤ that of ethane would be considered as non-VOC contributors. For nonhalogenated oxygenated compounds, only acetone, methyl acetate and *t*-butyl acetate have been exempted. Recent work indicates that only a handful of other common oxygenates could be exempted by this definition. These molecules have the right photochemical reactivity, and other solvent properties to positively address the VOC issue and offer the coatings industry options for formulating oil-based low VOC paints as water-based systems may produce other environmental issues in the nation's water systems.

## Summary and discussion

A systems approach clearly is the most effective way to manage the identification, evaluation and development of new products bringing environmental value. At the heart of new product development success is sound fundamental science and engineering along with a good understanding of the marketplace and of regulatory drivers. Each product discussed here was brought forward by employing some form of new product development process. We have discussed refrigerators/refrigerant oils, smog abatement via reformulated gasoline and via low (no) VOC containing coatings formulations, and environmental benefits (reduced fuel usage, less smog, and lower particulates) achievable through implementation of CAFE standards via superior fluids in passenger cars.

There will be a continuing need into the next century for evolutionary and revolutionary products/processes that will improve our environment. Some areas to consider are: biodegradable lubricants for hydraulic systems (which sometimes undergo leaks to the soil), diesel engine/fuel systems generating very low particulate emissions, cost and performance efficient fuel cell systems, possible alternatives for chemical intermediates such as phosgene (used to provide the CO moiety for polycarbonates, foams, etc.) and methyl isocyanate, new polymeric materials, new catalytic materials, and the list goes on and on. As noted earlier, looking at the overall system, remembering the driving force of environmental benefits, considering all aspects of environmental impact, and following best practices in the new product development process will maximize the likelihood of success.

## Literature cited


Blanpied, R. H., and J. D. Thornsberry, “Method of Producing Rigid Foams and Products Produced Therefrom,” U.S.Patent No. 5,978,652 (Nov. 26, 1996).

Carter, W. P., and R. Atkinson, “An Experimental Study of Incremental Hydrocarbon Reactivity,” *Environ. Sci. Techn.*, **21**, 670 (1987).

*Chemical Week*, “Health Concerns Dim Prospects for MTBE,” (Apr. 22, 1998).

Cooper, R. G., *Winning of New Products*, Addison-Wesley, Reading, MA(1993).

Executive Order (Mar. 25, 1999).

Hagihara, T., and A. Sakai, “Refrigerant Oil Composition Containing a Fluoroethane and an Ester Compound,” U.S. Patent No. 5,096,606 (Mar. 17, 1992); M. A. Krevalis, Jr., R. H. Schlosberg, and C. B. Duncan, “Refrigeration Working Fluid Compositions Containing Difluoroethane or Pentafluoroethane and a Polyolester Lubricant,” U.S. Patent No. 5,494,597 (Feb. 27, 1996).

Hounshell, D. A., and J. K. Smith, *Science and Corporate Strategy,* Cambridge University Press (1988).

*Montreal Protocol on Substances that Deplete the Ozone Layer* (1987).

*New York Times*, “Poison Gas Kills 100 in Cleveland Clinic” (May 16, 1929).

Rice, M. P., G. C. O’Connor, L. S. Peters, and J. G. Morone, “Managing Discontinuous Innovation,” *Res. Technol. Manage.*, 52 (May-June, 1998).

Rowland, F. S., and M. J. Molina, “Stratospheric Sink for Chlorofluoromethanes: Chlorine Atom-Catalysed Destruction of Ozone,” *Nature*, **249**, 810 (1974).

Schlosberg, R. H., H. S. Aldrich, L. D. Sherwood-Williams, J. S. Szobota, M. A. Krevalis, Jr., D. P. Leta, D. G. L. Holt, and F. H. Gordon, “Polyol Ester Compositions with Unconverted Hydroxyl Groups,” U.S. Patent No. 5,744,434 (Apr. 28, 1998).