INVITATION TO SUBMIT A RESEARCH PROPOSAL ON AN ASHRAE RESEARCH PROJECT

1884-TRP, The incorporation of odorants in refrigerants to improve leak detection (Experimental Phase III)

Attached is a Request-for-Proposal (RFP) for a project dealing with a subject in which you, or your institution have expressed interest. Should you decide not to submit a proposal, please circulate it to any colleague who might have interest in this subject.

Sponsoring Committee: TC 3.1, Refrigerants and Secondary Coolants Co-sponsored by: MTG for Low Global Warming Potential Refrigerants

Budget Range: \$150,000 may be more or less as determined by value of proposal and competing proposals.

Scheduled Project Start Date: April 1, 2023 or later.

All proposals must be received at ASHRAE Headquarters by 8:00 AM, EST, December 15, 2022. <u>NO</u> <u>EXCEPTIONS, NO EXTENSIONS.</u> Electronic copies must be sent to <u>rpbids@ashrae.org</u>. Electronic signatures must be scanned and added to the file before submitting. The submission title line should read: 1884-TRP, The incorporation of odorants in refrigerants to improve leak detection (Experimental Phase), and *"Bidding Institutions Name"* (electronic pdf format, ASHRAE's server will accept up to 10MB)

If you have questions concerning the Project, we suggest you contact one of the individuals listed below:

For Technical Matters:	For Administrative or Procedural Matters:
Technical Contact	Manager of Research & Technical Services (MORTS)
Marc Scancarello	Michael R. Vaughn
Emerson	ASHRAE, Inc.
1675 West Campbell Rd.	180 Technology Parkway, NW
Sidney, OH 45373	Peachtree Corners, GA 30092
Phone: 937-726-0668	Phone: 404-636-8400
E-Mail: marc.scancarello@emerson.com	Fax: 678-539-2111
-	E-Mail: MORTS@ashrae.net

Contractors intending to submit a proposal should so notify, by mail or e-mail, the Manager of Research and Technical Services, (MORTS) by December 1st, 2022 in order that any late or additional information on the RFP may be furnished to them prior to the bid due date.

All proposals must be submitted electronically. Electronic submissions require a PDF file containing the complete proposal preceded by signed copies of the two forms listed below in the order listed below. ALL electronic proposals are to be sent to rpbids@ashrae.org. All other correspondence must be sent to <u>ddaniel@ashrae.org</u> and <u>mvaughn@ashrae.org</u>. Hardcopy submissions are <u>not</u> permitted. In all cases, the proposal must be submitted to ASHRAE by 8:00 AM, EST, December 15, 2022. NO EXCEPTIONS, NO EXTENSIONS.

The following forms (Application for Grant of Funds and the Additional Information form have been combined) must accompany the proposal:

- (1) ASHRAE Application for Grant of Funds (electronic signature required) and
- (2) Additional Information for Contractors (electronic signature required) ASHRAE Application for Grant of Funds (signed) and

ASHRAE reserves the right to reject any or all bids.

State of the Art (Background)

The state-of-the-art to detect leaks is electronic leak detectors. However, they are new to the residential HVACR industry. Their reliability and lifespan are not precisely known. There are also concerns about false negative and false positive signals as well as calibration frequency. With that said, much work is currently underway to resolve these sensor performance questions, and the results are forthcoming. Considering this uncertainty, due diligence dictates the consideration of odorants.

Until now, there has not been a strong motivation to odorize refrigerants because the previous and current refrigerants for occupied spaces were mostly non-flammable. The ability to smell a leak would not only benefit the consumer, but would also create a safer working environment for the HVACR manufacturer and field service personnel. A legacy example where an odor has had a benefit is with ammonia, which of course is naturally odorized. The pungent smell of ammonia has likely saved lives. In Europe, Propane has been used in refrigeration systems for many years without an odorant, but the refrigerant charge has been intentionally limited to 57-150 grams. However, there are discussions in Standards committees today that are allowing larger refrigerant charge limits for both A2L and A3 flammable refrigerants. Some of the ways larger charges are being justified are by using leak detection sensors, room size restrictions, solenoid valves to limit the releasable charge and emergency ventilation mitigation. Odorizing would be one more way to help assure public safety.

This research is justified because there are many technical challenges associated with the use of odorants in HVACR. One reason is the concern that odorant additives would not be chemically stable inside a complex hermetically sealed unit for the life of the system. There are many challenging conditions, such as: Temperature and pressure extremes, phase changes and preferential solubility in the lubricant. Other concerns are system efficiency effects, valve clogging or degradation of the materials-of-construction. However, many of these concerns are hypothetical in nature and/or based on the attempts made to odorize older refrigerants, such as CFC's and HCFC's. A comprehensive study has yet to be done with the newer Low Global Warming Potential refrigerant compositions. These new refrigerants and their associated oils may react more favorably to odorization.

Key and ancillary references are cited and two patents are listed.

Justification and Value to ASHRAE

There are many technical committees, standards committees, research and MTG's within ASHRAE working toward implementing flammable low global warming refrigerants. This study is equally important, and its aim is precisely aligned with these other efforts. ASHRAE's members will undoubtedly benefit from this research since it is rooted in improving public safety.

This study would apply to the following 2010-2018 ASHRAE Research Plan goals:

<u>Plan Goal 8</u>: Facilitate the use of natural and low global warming potential (GWP) synthetic refrigerants and seek methods to reduce their charge

Objectives

1 - Effectively incorporate natural and low GWP synthetic refrigerants in Air Conditioning & Refrigeration (AC&R) equipment.

Technical Challenges

1 - Use of natural refrigerants that are identified as toxic or flammable by regulatory authorities.

Needed Research 9

Develop basic data to support industry risk assessments to determine what types of applications can use flammable or toxic refrigerants safely and what system modifications could be made to improve safety.

Potential Co-Funding: None

Objectives

To empirically determine if odorants can satisfy the requirements set forth herein by examining both the fundamental properties of the refrigerants and oils using standardized bench tests as well as how well they perform

in a system, including detectability. It is not the intent of this research to broadly approve odorants for all refrigerants and applications or equipment. The objective is to use a couple of proxy systems and conditions with the goal of giving the industry an 'initial assessment' about the efficacy of odorant feasibility.

If no current-day odorant passes this experimental screening, it may inspire other researchers to invent a new odorant molecule for the HVAC&R industry. The invention of new odorants is not within the scope of this study.

Scope:

The testing shall be phased (gated with milestones) in terms of both money outlay and effort. The project may be halted at any point if the PMS deems it necessary based on the results. Phases 1 and 2 are complete. ASHRAE funded Phase 1 and the Consumer Products Safety Commission funded Phase 2. It is the intent that ASHRAE fund Phase 3 (current Phase) and Phase 4 will be considered later, pending the results of phase 3.

Phase No.	Approx. Dur	ation *Task/Milestone (See below for details)	Status
1.	(Mos.) 3	 -White Paper Study -Confirm final down-selected list of odorants, refrigerants and o -Determine odorant threshold concentration ranges to test for each. 	ils <i>COMPLETED</i> (ASHRAE funded)
2.	3	-Perform ASHRAE Std. 97 Chemical Stability Screening on 36 samples.	COMPLETED (CPSC funded)
3.	8	-Systems Testing -Using a system circuit with an evaporator, condenser and line-s determine: The odorizing effectiveness over time, the odorant concentration distribution around the circuit and within the refrigerant vs. the oil.	et, CURRENT RFP
4.	3	Systems performance testing, Materials Compatibility testing	TBD

Test Matrix Summary:

Refrigerant/Lubricant	Odorant		
	Dimethyl Sulfide,	Methyl Ethyl Sulfide,	Trimethylamine,

	150 ppm	150 ppm	50 ppm
R32/PAG	Y	Y	N
R32/POE	Y	Y	Ν
R32/PVE	Y	Y	Ν
R1234yf/PAG	Y	Y	Y
R1234yf/POE	Y	Ν	Y
R1234yf/PVE	N	Ν	Y
R290/PAG	Y	Y	Y
R290/POE	Y	Y	Y
R290/PVE	Y	Ν	Ν

*The following are more detailed descriptions of the tests shown above. The lighter font text are for projects already completed or planned for the future.

1 -To determine whether the list of down-selected odorants from the prior ASHRAE RP 1794 is complete and accurate. The contractor should assure that the toxicity of the odorants at the concentrations being considered is acceptable and safe. Both outside resources (from any new information) and the prior ASHRAE RP1794 study should be considered. Three refrigerants shall be tested (a single component A2L, an A2L blend and one hydrocarbon, likely propane). Two odorants each for the A2L's and 5 odorants each for the A3 shall be tested. Two oils shall be tested for each refrigerant. Also, two concentrations of odorants shall be PMS. Odorant concentration determination: This effort will include identifying the concentration range of odorant needed that is released from the refrigerant and oil mixture which an operator is able to detect (and identifying the concentration which an operator is barely able to detect), so two concentration values. Evaluate effective vapor concentration methods using applicable analytical techniques for use in downstream odorant distribution assessments.

2 - Chemical Stability Screening: This effort will include sealed pressure vessel testing (ASHRAE Std. 97) to evaluate the impact of the odorants on the chemical and thermal stability of the mixture (refrigerant+lubricant+odorant+metal catalysts). 36 samples described in (1) above shall be tested. A replicate of three for each combination (as per ASHRAE Std. 97) shall be performed (3 x 36 total sealed pressure vessels). Stability of both the odorant itself and its effect on the refrigerant and lubricant shall be assessed.

Phase 3. Systems Testing

Odorant Distribution and Effectiveness over Time: Since it is important to assure that during a refrigerant leak the odorant concentration is sufficient to be detected via smell, understanding the uniformity-of-concentration within the refrigeration circuit is critical. Therefore, in this research, the odorant concentration must be measured at locations within the circuit that allow analysis of: The oil itself, the vapor refrigerant (or mostly vapor) and the liquid refrigerant. The sampling orifice should be small enough to simulate a leak in a real system (perhaps the size of a capillary tube). It is required that an actual refrigerant circuit with a operating condenser and evaporator be used. Either a laboratory bench set-up loop, a trainer system or a production OEM unit may be used. A stable AHRI standard running condition shall be chosen where the system cycles on-andoff. The chemical analytical method chosen must have sufficient sensitivity to detect PPM levels of the odorants.

Likewise, it is important to understand if the odorant lasts sufficiently long in a working system or does it 'fade' with time. This effort will include measurement of odorant concentration in the refrigerant vapor phase once it has been used in refrigeration loop for an extended period. This task will also help determine the quantity of odorant to be initially added to a particular real system. The pipe walls and other system components (including the oil) may absorb the odorant and render it less effective because of its reduced concentration in the refrigerant. A filter drier shall not be used for this study. The test shall be terminated if the odorant concentration falls below the documented and accepted threshold for human detection for that particular odorant.

4 - Materials Compatibility testing (Not currently funded by ASHRAE): This effort will include performing the compatibility tests between the odorants and certain standard HVAC&R materials-of-construction, such as brass, copper, rubber seals, nylon and other polymers and potentially some reactive process chemicals, such as tube forming lubricants. These tests will address issues related to solvation, crazing, embrittlement, corrosion and any reactions due to addition of odorant in the refrigerant. This would only be a cursory study with common materials. It is anticipated that the current AHRTI/DOE MCLR project will fund this tested for every sample. This yields 36 total refrigerant/odorant/oil combinations. The specific refrigerants and oils shall be chosen by the part.

Note: Safe practices will need to be followed by the contractor when dealing with all flammable refrigerants and the odorants.

Some standard tests which may be used for the above activities are listed below:

- ASTM E679-19, Standard Practice for Determination of Odor and Taste Threshold by a Forced-Choice Ascending Concentration Series Method of Limits, American Society for Testing and Materials, Philadelphia, PA: 1991.
- ASTM E544-18, Standard Practice for Suprathreshold Odor Intensity Measurement, American Society for Testing and Materials, Philadelphia, PA: 1999.
- ASHRAE Standard 97 Sealed Glass Tube Method to Test the Chemical Stability of Material for Use within Refrigeration Systems
- AHRI 340/360: Performance Rating of Commercial and Industrial Unitary Air-Conditioning and Heat Pump Equipment

Deliverables:

1. Contractor will meet with the Project Monitoring Subcommittee (PMS) to kick-off the project and confirm understanding of the goals and the details of the work statement. This may be done via teleconference.

2. The contractor will prepare a project plan with a time-line. This may be in the form of a presentation. The PMS

- will review this and discuss any other remaining issues with the contractor. This may be done via teleconference.
- 3. Intermediate report 1: The contractor shall prepare a presentation.
- 4. Intermediate report 2: The contractor shall prepare a presentation.
- 5. Intermediate report 3: The contractor shall prepare a presentation.
- 6. The contractor shall prepare a final presentation.

Progress, Financial and Final Reports, Technical Paper(s), and Data shall constitute the deliverables ("Deliverables") under this Agreement and shall be provided as follows:

a. Progress and Financial Reports

Progress and Financial Reports, in a form approved by the Society, shall be made to the Society through its Manager of Research and Technical Services at quarterly intervals; specifically on or before each January 1, April 1, June 10, and October 1 of the contract period.

The following deliverables shall be provided to the Project Monitoring Subcommittee (PMS) as described in the Scope/Technical Approach section above, as they are available:

Furthermore, the Institution's Principal Investigator, subject to the Society's approval, shall, during the period of performance and after the Final Report has been submitted, report in person to the sponsoring Technical Committee/Task Group (TC/TG) at the annual and winter meetings, and be available to answer such questions regarding the research as may arise.

b. Final Report

A written report, design guide, or manual, (collectively, "Final Report"), in a form approved by the Society, shall be prepared by the Institution and submitted to the Society's Manager of Research and Technical Services by the end of the Agreement term, containing complete details of all research carried out under this Agreement, including a summary of the control strategy and savings guidelines. Unless otherwise specified, the final draft report shall be furnished, electronically for review by the Society's Project Monitoring Subcommittee (PMS).

Tabulated values for all measurements shall be provided as an appendix to the final report (for measurements which are adjusted by correction factors, also tabulate the corrected results and clearly show the method used for correction).

Following approval by the PMS and the TC/TG, in their sole discretion, final copies of the Final Report will be furnished by the Institution as follows:

-An executive summary in a form suitable for wide distribution to the industry and to the public. -Two copies; one in PDF format and one in Microsoft Word.

c. Science & Technology for the Built Environment or ASHRAE Transactions Technical Papers

One or more papers shall be submitted first to the ASHRAE Manager of Research and Technical Services (MORTS) and then to the "ASHRAE Manuscript Central" website-based manuscript review system in a form and containing such information as designated by the Society suitable for publication. Papers specified as deliverables should be submitted as either Research Papers for HVAC&R Research or Technical Paper(s) for ASHRAE Transactions. Research papers contain generalized results of long-term archival value, whereas technical papers are appropriate for applied research of shorter-term value, ASHRAE Conference papers are not acceptable as deliverables from ASHRAE research projects. The paper(s) shall conform to the instructions posted in "Manuscript Central" for an ASHRAE Transactions Technical or HVAC&R Research papers. The paper title shall contain the research project number (1884-RP) at the end of the title in parentheses, e.g., (1884-RP).

All papers or articles prepared in connection with an ASHRAE research project, which are being submitted for inclusion in any ASHRAE publication, shall be submitted through the Manager of Research and Technical Services first and not to the publication's editor or Program Committee.

d. Data

Data is defined in General Condition VI, "DATA"

e. Project Synopsis

A written synopsis totaling approximately 100 words in length and written for a broad technical audience, which documents 1. Main findings of research project, 2. Why findings are significant, and 3. How the findings benefit ASHRAE membership and/or society in general shall be submitted to the Manager of Research and Technical Services by the end of the Agreement term for publication in ASHRAE Insights

The Society may request the Institution submit a technical article suitable for publication in the Society's ASHRAE JOURNAL. This is considered a voluntary submission and not a Deliverable. Technical articles shall be prepared using dual units; e.g., rational inch-pound with equivalent SI units shown parenthetically. SI usage shall be in accordance with IEEE/ASTM Standard SI-10.

Level of Effort

Approx. Funding amount: \$150,000 Professional Months: Total: Est. 12 months

Proposal Evaluation Criteria

Proposals submitted to ASHRAE for this project should include the following minimum information:

No.	Proposal Review Criterion	Weighting Factor
1	Contractor's understanding of Work Statement as revealed in proposal.	10%
	a) Logistical problems associated	
	b) Technical problems associated	
2	Quality of methodology proposed for conducting research.	20%

	a) Organization of project	
	b) Management plan	
3	Contractor's capability in terms of facilities.	20%
	a) Managerial support	
	b) Data collection and c) Technical expertise	
4	Qualifications of personnel for this project.	30%
	a) Project team 'well rounded' in terms of qualifications and experience in related work	
	b) Project manager person directly responsible; experience and corporate position	
	c) Team members' qualifications and experience	
	d) Time commitment of Principal Investigator	
5	Probability of contractor's research plan meeting the objectives of the Work Statement.	15%
	a) Detailed and logical work plan with major tasks and key milestones	
	b) All technical and logistic factors considered	
	c) Reasonableness of project schedule	
6	Performance of contractor on prior ASHRAE or other projects	5%

Project Milestones

No.	Major Project Completion Milestone	Deadline Month
1	-Confirm final down-selected list of odorants, refrigerants and oils -Determine odorant threshold concentration ranges to test for each.	3 months
2	Perform ASHRAE Std. 97 Chemical Stability Screening on 36 samples.	3 months
3	Using a system circuit with an evaporator and condenser, determine: The odorant effectiveness over time, the odorant concentration distribution around the circuit and the impact of the odorant addition on the system performance.	4 months
4	Material Compatibility tests (if DOE funding approved)	3 months

Key References

- 1. ASHRAE Odorant White Paper Study, RP1794.
- 2. ASHRAE 2022 Winter Conference, Session 4 Presentation, System Stability and Contaminant Control with Lower GWP Refrigerants, "Compatibility of Odorants with Refrigerants and Lubricants"
- 3. US Patent 6,581,404B2, Refrigerant (Sanyo, June 24, 2003)
- 4. US Patent 1,905,817, Odorant for Refrigeration (Roessler and Hasslacher Chemical Company, Apr. 25, 1933)
- 5. Patent US4294716A granted 13-Oct-1981. "Halocarbon and azeotrope refrigerant compositions containing offensive warning component" http://www.google.com/patents/US4294716

Other miscellaneous related references:

- 1. Engle, K.-H., R. A. Flath R. G. Buttery, T.R. Mon, D. W. Ramming and R. Teranishi, J. Agric. Food Chem., 36, 549-553 (1988)
- 2. Takeoka, G. R., R. A. Flath, T. R. Mon, R.Teranishi and M. Guentert, J. Agric. Food Chem., 38, 471-477 (1990)

3. Shaw, P E., J. Tatum, T. Kew, C. Wagner Jr. and R. Berry, J. Agric. Food Chem., 18, 343-345 (1970)

- 4. Fors, S. "Sensory Properties of Volatile Maillard Reaction Products And Related Compounds- in The Maillard Reaction in Foods and Nutrition, ACS Symposium Series 215, G. R. Waller and M. S. Feather, Editors, ACS, Washington, pp. 185-286 (1988)
- 5. Mulders, J., Z. Lebensm. Unters. Forsch., 151, 310-317 (1973)
- 6. Hartung, L D., E. G. Hammond and J. R. Minor Livestock Waste Management Pollution Abatement, Int. Symp. Proc., 105-106 (1971)
- 7. Flath, R. A., D. R. Black, D. G. Guadagni, W. H.McFadden and T. H. Schultz, J. Agric. Food Chem., 15, 2935 (1967)
- 8. S. Harrison, C. J., Inst. Brewing, 76, 486-495 (1970)
- 9. Mielgard, M. Master Brew. Assn. Am. Tech. Quart., 12(3), 151-168 (1975)
- 10. Buttery, B. G., J. G. Turnbaugh and L. C. Ling, J. Agric. Food Chem., 36(5) 1006-1009 (1988)

- 11. Guadagni, G., R G. Buttery and S. Okano J. Sci. Food Agric., 14, 761-765 (1963)
- 12. Amoore, J. E., L. J. Forrester and P. Pelosi, Chem Senses & Flavor, 2(1), 17-25 (1976)
- 13. Fazzalari, F A., editor, Compilation of Odor and Taste Threshold Data, ASTM Data Series DS 48A (1978)
- 14. Lea, C. H., and P. A. T. Swoboda, Chem Ind. (London), 1289-1290 (1958)
- 15. Siek, T. J., I.A. Albin, L. A. Sather and R. C. Lindsay, J. Food Sci., 34, 265 (1969)
- 16. Day, E. A., D. A. Lillard and M. W. Montgomery J. Dairy Sci., 46, 291-294 (1963)
- 17. Amoore, J, E. L. J. Forrester and R. G. Buttery, Chem. Ecol., 1, 299-310 (1975)
- 18. Griffiths, N. M., Chem. Senses Flavor, 1, L87 (1974); abstracted from reference 13.
- 19. Baker, B. A., J. Am. Water Works, 55, 913-916 (1963)
- 20. Kieth, E. and J, Powers, J. Food Sci., 33, 213-218 (1968)
- Buttery, R. G. B. M. Seifert, D. G. Guadagni, D. R. Black and L. C. Ling, J. Agric. Food Chem., 16,1009-015(1968)
- 22. Golovnja, R. V and M. Rothe, Nahrung, 24, 129-139 (1980)
- 23. Guadagni, D. G., Am. Perf. Cosm., 82, 43 (1967)
- 24. Lindsey, R. C., J. Dairy Sci., 52,1198 (1969); abstracted from reference 1:3.
- 25. Wick, E. L., Food Technology, 20, 1549 (1966); abstracted from reference 13.
- 26. Patton, S., Food Research, 22, 316 (1957); abstracted from reference 13.
- 27. Salo, P., J. Sci. Food Agric., 21, 597 (1970); abstracted from reference 13.
- 28. Guadagni, D. G., R. G. Buttery and J. Harris, J. Sci. Food Agric., 17, 142-144 (1966)
- 29. Amoore, J. E. and D. Venstrom, J. Food Sci., 31, 118-128 (1966)
- 30. Wasserman, A. E., J. Food Sci., 31, 1005 (1966); abstracted from reference 13.
- 31. Boehlens, M. H. and J. van Gemert, Perfumer & Flavorist, 12(5), 31-43 (1987)
- 32. Guadagni, D. G., R. G. Buttery and J. Turnbaugh, J. Sci. Food Agric., 23, 1435-1444 (1972)
- 33. Meijboom, P W, J. Am. Oil Chem. Soc., 41, 326-328 (1964) References
- van Gernert, L. J. and A. H. Nettenbreijer, Editors, Compilation of Odor Threshold Values in Air and Water; RID, CIVO-TNO, Zeist, The Netherlands (1977)
- 35. Patton, S., J. Food Sci., 29, 679 (1964)
- 36. Sega, G. M., M. J. Lewis and M. H. Woskow, Proc. Am. Soc. Brew. Chem., 156-164 (1967)
- Ohloff ' G., "Recent Developments in the Field of Naturally Occurring Aroma Components", Prog. Chem. Org. Nat. Prod., 35, 431-527 (1978)
- 38. Amoore, J. E., Chem. Senses Flavor, 2(3), 267-281 (1976)
- 39. Palamand, S.R. and W.A. Hardwick, Master Brewing Assn., Am. Tech. Quart., 6, 117-128 (1968)
- 40. Pietrzak, E.W.A., Acta Aliment. Polonia, 2, 207 (1976); abstracted from reference 13.
- 41. Patton, S.J., Dairy Sci., 37, 446-452 (1954)
- 42. Manning, D. J., J. Dairy Res., 40, 6:3,73 (1973); abstracted from reference 13.
- 43. Takeoka, G., R.G.. Buttery, R. A. Flath, R. Teranishi, E. L. Wheeler, R. L. Wieczorek & M.
- Guentert, "Volatile Constituents of Pineapple" in Flavor Chemistry: Trends and Developments, ACSymp. Series 388, R. Teranishi R. G. Buttery and F. Shahidi editors, ACS, Washington DC, pp. 221
- 237 (1989)
- 44.Cartwright, L. C., Food Technology, 6, :372 (1952); abstracted from reference 13.
- 45. Buttery, B. G., B. M. Siefert, D. C. Guadagni and L. C. Ling, J. Agric. Food Chem., 19, 524-529 (1971)
- Buttery, R. G., R. Teranishi, R. A. Flath and L. C. Ling "Fresh Tomato Volatiles" in Flavor Chemistry: Trends and Developments, ACS Symp. Series 388, R. Teranishi, R. G. Buttery and F. Shahidi, editors, ACS, Washington, DC, pp. 211-222 (1989)
- 47. Wysocki, C. J. and A. N. Gilbert, Ann. New York Acad. Sci., 561, 12-28 (1989)
- 48. Collins, I., J. Agric. Food Chem., 19, 533-535 (1971)
- 49. Tressl, R., Monatsschr. Brau., 32(5), 240-248 (1979)
- 50. Rosen, A. A., J. Water Pollut. Control Assn., 35, 777 (1963); abstracted from reference 13.
- 51. Koehler, P. E., M. E. Mason and G. V Odell, J. Food Sci., 36, 816-818 (1971)
- 52. Buttery, R.G., R. M. Seifert, D. G. Guadagni and L. C. Ling, J. Agric. Food Chem., 17, 1322-1327 (1969)
- 53. Brule, G., P. Dubois and T. Obretenov, Ann. Technol. Agric., 20, 305-312 (1971)
- 54. Bergia, H. W., Food Technology, 9, 23 (1955): abstracted from reference 13.
- 55. Kirimura, J., J. Agric. Food Chem., 17, 689 (1969): abstracted from reference 13.
- 56. Land, D. G., Referenced in ASTM Data Series DS 48A (ref. 1:3)
- 57. Swan, J. S. and S. M. Burtles, Chem. Soc. Rev., 7(2), 201-211 (1978)
- 58. Pittet, A., P. Rittersbacher and R. Muralidhara J. Agric. Food Chem. 18, 929-933 (1970)

- 59. Schutte, L., CRC Crit. Rev. Food Technol., 4, 457-505 (1974); see also ref. 104
- 60. Hoehn E., As referenced in ASTM Data Series DS 48A (ref. 13)
- Vernin, G. and G. Vernin, "Heterocyclic Aroma compounds in Foods: Occurrence and Organoleptic Properties" In "The chemistry of heterocyclic flavoring and aroma compounds", G. Vernin, editor, Ellis Horwood Ltd., Chichester, England, pp. 72-150 (1982)
- 62. Amoore, J. E., J. R. Popplewell and D. Whissell-Buechy, J. Chem. Ecol., 1, 291-297 (1975) References
- 63. Leonardos, G., L. M. Libbey, NV. Y. Cobb and E. A. Day, J. Air Pollution Control Assn., 19, 91-95 (1969)
- 64. Maga, J. A., Cereal Foods World, 18, 326 (1973); abstracted from reference 13.
- 65.Rothe, M., C. Wolm, L. Tunger and H. J. Siebert, Nahrung, 16, 483 (1972); Chem. Abstr. 78, 15568c (1973)
- 66. Griffiths, N. H., Nature, 243, 304 (1973)
- 67. Tatum, J. H., J. Food Sci., 40, 707 (1973); abstracted from reference 13.
- 68. Forss, D. A., "Odor and Flavor Compounds from Lipids" in Progress in the chemistry of fats and other lipids, Vol. XIII, Part 4, R. T. Holmann, editor, Pergamon Press, Oxford, p. 117 (1972)
- 69. Teranishi, R., R. Buttery and D. Guadagni, Geruch-und Geschmackstuffe, Proc. Int. Symp. Bad Pyrmont, F.Drawert, editor, Verlag Hans Carl, Nurumberg, pp. 177-186 (1975)
- Pickenhagen, W, "Enantioselectivity in Odor Perception" in Flavor chemistry: Trends and Developments, ACS Symp. Series 388, R. Teranishi, R. G. Buttery and F. Shahidi, editors, ACS, Washington DC, pp. 151-157 (1989)
- Peyron, L., "Recent Techniques in the Analysis of Heterocyclic Aroma Compounds in Food" in "The chemistry of heterocyclic flavoring and aroma compounds", G. Vernin, editor, Ellis Horwood Ltd., Chichester, England, pp. 262-304 (1982)
- 72. Walker, N. and I. Gray, J. Agric. Food Chem., 18, 346-352 (1970)
- 73. Sick, T. J., J. A. Albin, L. A. Sather and R. C. Lindsey J. Dairy Sci., 54, 1 (1971)
- 74. Anon, Givaudan Corporation, Product Data Sheet, 1986
- 75. Pyysalo, T., Materials and Processing Technology, Tech. Res. Center of Finland, Pub. 14, Helsinki (1976)
- 76. Takken, H., L. van der Linde, M. Boehlens and J. van Dort, J. Agric. Food Chem., 23, 638-642 (1975)
- 77. Tressl, R., B. Renner, T. Kossa and H. Koppler European Brew. Conv., Proc. 16th Congress, 693-707 (1977)
- 78, Seifert, R. M., R.G. Buttery, D. G. Guadagni, D. Black and J. Harris, J. Agric. Food Chem., 18, 246-249 (1970)
- 79. Deck, R. E. and S. S. Chang, Chem. Ind. (London), 1343-1344 (1975)
- 80. Vernin, G., Parfums. Cosmet. Aromes, 29 (June/July), 77-87 (1979)
- 81. Buttery, R. G., D. G. Guadagni and R. Lundin, J. Agric. Food Chem., 24, 1-3 (1976)
- 82. Honkanen, E., Acta Chem. Scand., 18, 612 (1964)
- Buttery, R. G., R. M. Seifert, L. C. Ling, E. L. Soderstrom, J. M., Ogawa and J. G. Turnbaugh, J. Agric. Food Chem., 30, 1208-1211 (1982)
- 84. Evans, C. D., H. A. Moser and C. D. List, J. Am. Oil Chem. Soc., 48, 495-498 (1971)
- Tressl R., "Formation of Flavor Components in Roasted Coffee" in "Thermal generation of aromas", ACS Symp. Series 409, T. H. Parliment, R. J., McGorrin and C.-T. Ho, editors, ACS, Washington DC, pp. 285-301 (1989)
- 86. Ohloff, G., Perfumer and Flavorist, 1(3), 11-22 (1978)
- 87. McGill, A. S., R. Hardy and J. R. Burt, J. Sci. Food Agric., 25, 1477 (1974)
- 88. Buttery, R. G., R. Teranishi, L. C. Ling and J. G. Turnbaugh, J. Agric. Food Chem., 38, 336-340 (1990)
- 89. Kazeniac, S. J. and R. M. Hall, J. Food Sci., 35, 519-530 (1970) References
- Kobayashi, A., "Sotolon Identification, Formation and Effect on Flavor" in Flavor Chemistry: trends and development, ACS Symp. Series 388, R., Teranishi, R. G. Buttery and F. Shahidi, editors, ACS, Washington DC, pp. 49-59 (1989)
- 91. Murray, K., J. Shipton and F. Whitfield, Chem. Ind. (London), 897-898 (1970)
- 92. Callabretta, P, Cosm. Perf., 90 (June), 74-80 (1975)
- 93. Mulders, E. J., R. J. C. Kleipool and M. C. ten Noever de Brauw, Chem. Ind. (London), 613-614 (1976)
- 94. Schieberle, P. and W. Grosche, "Bread Flavor" in Thermal generation of aromas, ACS Symp.
- Series 409, T. H. Parliment, R. J. McGorrin and" C.-T. Ho, editors, ACS, Washington DC, pp, 258-267 (1989)
- 95. Boehlens, M., P. de Valois, H. Wobben and A. van der Gen, J. Agric. Food Chem., 19, 984-991 (1971)
- 96. Callabretta, P, Perfumer and Flavorist, 3(3),33-42 (1978)
- 97, Teranishi, R., "Odor and Molecular Structure" in Gustation and Olfaction, G. Ohloff and A. F. Thomas, ed., pp.] 65177 (1971)
- 98. Seifert, B. M., et. al., J. Sci. Food Agric., 26, 1844 (1975)
- 99. Berry, B. E., C. J. Wagner, Jr., and M. G. Moshonas J. Food Sci., 32, 75 (1,967)
- 100. Stark, W. an(] D. A. Forss, J. Dairy Res., 31,253 (1964)

- 101. Engen, S., J. Inst. Brew. Assn., 80, 162 (1974); abstracted from reference 13.
- 102. Buttery, R. G., L. C. Ling, R. Teranishi and T. Mon, J. Agric. Food Chem., 25, 1227-1229 (1977)
- 103. Schmidlin-Meszaros, J., Alimenta, 10, 39 (1971)
- 104. Schutte, L. "Precursors of Sulfur-Containing Flavor Compounds" in Feneroli's Handbook of Flavor Ingredients, T. E. Furia and N. Bellanca, editors, CRC Press.
- 105. Mussinan, C. J., R. A. Wilson, I. Katz, A. Hruza and M. H. Vock, "Identification and Flavor Properties of Some 3-Oxazolines and 3-Thiazolines Isolated From Cooked Beef" in "Phenolic, sulfur, and nitrogen compounds in food flavor", ACS Symp. Series 26, G. Charalambous and I. Katz, editors, ACS, Washington DC, 1976
- 106. Demole E., P Enggist and G. Ohloff, Helv. Chem. Acta, 65, 1785-1794 (1982)
- 107. Urbach, G., J. Dairy Res., 39, 42 (1972); abstracted from reference 13.
- 108. Buttery, R. C., R. Teranishi, R. A. Flath and L. C. Ling, J. Agric. Food Chem., 38, 792-795 (1990)
- 109. Nishimura, O. and S. Mihara, J. Agric. Food Chem., 38, 10381041 (1990)
- 110. Flament, I., Food Rev. Int., 5(3), 317-414 (1989)
- 111. Buttery, R., D. Guadagni, L. Ling R. Seifert and W. Lipton, J. Agric. Food Chem., 24, 829-832 (1976)
- I 12. Cain, W. S. and J. C. Stevens, Annals New York Acad. Sci., 561, 29-38 (1989)
- 113. Cowart, B., J. Annals New York Acad. Sci., 561, 39-55 (1989)
- 114. Doty, B. L., Annals New York Acad. Sci., 561, 76-86 (1989)
- 115. Stevens, J. C., Annals N ew York Acad. Sci., 561, 87-93 (1989)
- 116. Schiffman, S. and M. Pasternak, J. Gerontol., 34, 73-79 (1979)
- 117. Schiffman, S. and J. C. Leffingwell, Pharmacol. Biochem. Behav., 14, 787-798 (1981)
- 118. Koelega, H. S. and E. P Coster, Annals New York Acad. Sci., 237, 234-346 (1974)
- 119. Koster E. P., Perfumer and Flavorist, 15(2).1-12(1990) References
- 120, Teranishi, R., R. G. Buttery and D. G. Gaudagni, Annals New York Acad. Sci., 237, 209-216 (1974)
- 121. Guadagni, D, G., R. G. Buttery, S. Okano and H. K. Burr, Nature (London), 200, 1288-1289 (1963)
- 122. Guadagni, D.G., and R. G. Buttery, J. Food. Sci., 43, 13461347 (1978)
- 123. Amoore, J. E., Molecular basis of odor, Charles C. Thomas, Springfield, IL, pp. 16-25 (1970)
- 124. Masuda, 11. and S. Mihara, J. Agric. Food Chem., 36, 584587 (1988)
- 125. Threshhold detection values abstracted from a more extensive list included in FlavorBase 98. "Flavor-Base" is a trademark of Leffingwell & Associates
- 126. US Patent 6,581,404B2, Refrigerant (Sanyo, June 24, 2003)
- 127. US Patent 1,905,817, Odorant for Refrigeration (Roessler and Hasslacher Chemical Company, Apr. 25, 1933)
- 128. US Patent 4,294,716A, "Halocarbon and azeotrope refrigerant compositions containing offensive warning component", (13-Oct-1981). http://www.google.com/patents/US4294716
- 129. US Patent 8,418,530B1, Compositions and Methods for Detecting leaks in HVAC/R Systems, (Mainstream Engineering Corp., Apr. 16, 2013)
- 130. EU Patent EP 1 094 100 A1, Refrigerant Composition, Closed Electric Compressor, and Refrigerator, (Matsushita, 25.04.2001)